PRODUCTION OF MANGANESE SLAGS FOR MANUFACTURING HIGH-GRADE FERROMANGANESE BY BLOWING OXIDATION SPIEGELEISEN

By Theodore Kootz and Jacob Willems, in cooperation with Willy Oelsen and Hanns Wentrup (Translated by Roy W. Tindula)

With Preface By Russell C. Buehl

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by

Theodore Kootz[2/] and Jacob Willems[2/], in cooperation with
Willy Oelsen and Hanns Wentrup[3/]
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1/ Translated from Stahl u. Eisen, vol. 70, No. 9, Apr. 27, 1950, pp. 360-369.
2/ Duisburg-Hamborn.
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PREFACE

Over 700,000 tons of manganese a year is needed by the United States steel industry. Unfortunately, about 90 percent of this manganese is produced from ores imported from distant countries, such as India, Union of South Africa, Gold Coast, French Morocco, and Brazil. There are only small domestic deposits of high-grade manganese ore or ore that can be treated by mechanical beneficiation to yield a material suitable for the production of standard ferromanganese. Consequently, imports of manganese ore insufficient to meet the needs of the steel industry will necessitate production of a suitable grade of ferromanganese from domestic manganiferous iron ores or steel-plant slags.

When such ores or slags are smelted, the resulting metal, usually designated as spiegeleisen, contains approximately 20 percent manganese, a much lower manganese content than standard 80-percent ferromanganese. The spiegeleisen often has too high a phosphorus content for use as an alloying or deoxidizing agent in steel production. Consequently, it is necessary to find a process for separating the manganese contained in domestic resources from excessive amounts of iron and phosphorus.

Methods for selective oxidation and selective reduction[5] as means for recovering manganese from low-grade manganese-bearing materials were investigated by the Bureau of Mines during and immediately following World War I.[6-8]

Germany experienced a shortage of manganese ores during World War II similar to that which now exists in the United States. A large amount of experimental research and large-scale operations were carried out to produce a synthetic manganese ore by selective oxidation of manganese from spiegeleisen in converters lined with basic refractories. An excellent review of the work done in Germany is contained in the article of Theodore Kootz and Jacob Willems from which this report was translated.

5/ Weld, C. M. and Others, Manganese: Uses, Preparation, Mining Costs, and the Manufacture of Ferro-Alloys, Bureau of Mines, Bulletin 173, 1930, 209 pp., 13 figs.

6/ Joseph, T. L., Royster, P. H., and Kinney, S. P., Utilization of Manganiferous Iron Ores: Bureau of Mines Tech. Paper 393, 1926, 28 pp.

7/ Joseph, T. L., Wood, C. E., and Barrett, E. P., The Production of High-Manganese Slag in the Electric Furnace: Bureau of Mines Rept. of Investigations 3080, 1930, 9 pp.

8/ Herty, C. H., Jr., Conley, J. E., and Royer, M. B., A Study of High-Manganese Slags in Relation to the Treatment of Low-Grade Manganiferous Ores: Bureau of Mines Tech. Paper 523, 1932, 36 pp.

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The Bureau of Mines is now engaged in extensive work on recovery of manganese from open-hearth slags in cooperation with the American Iron and Steel Institute. A major phase of this work is concerned with selective oxidation of manganese from spiegeleisen in basic converters. It is believed that this translation will aid those interested in the commercial application of the process to evaluate the merits of the methods as practiced in Germany, as well as new developments resulting from the work of the Bureau of Mines.

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INTRODUCTION

Manufacture of high-grade ferromanganese, as a rule, requires a low-phosphorus manganese ore with 45 to 55 percent Mn, chiefly obtained in the Soviet Union, the British Dominions, and Brazil. Also, low-manganese ores have already been used for ferromanganese production, especially in North America and Germany. During World War I, a process was developed in which a high-phosphorus ferromanganese or spiegeleisen was prepared in the blast furnace from low- or high-phosphorus manganiferous ores, then low-phosphorus manganese slag was prepared by refining under an acid slag, and this material was worked into a low-phosphorus ferromanganese in the blast furnace.9/

Manufacture of useful manganese ores from a phosphorus-bearing spiegel with 12 to 15 percent Mn, 4.5 percent C, and 0.5 percent P by slagging in a refining furnace was reported by Joseph, Barrett, and Wood.10/ The spiegel was refined to 0.75 percent Mn, 3.4 percent C, and 0.45 percent P. Thereby, a slag with about 43 to 58 percent Mn and about 10 percent SiO_2 was obtained. Hotter melts gave a smaller phosphorus content in the slag than cold melts. In addition, the phosphorus content of the slag varied with the manganese content of the intermediate metal.

Blowing of low-phosphorus spiegel in the converter was reported in a session of the Steel Works Committee of the Association of German Steel Producers by H. Bansen and J. Wittig on January 19, 1937.11/ A spiegel with 12 to 20 percent Mn was refined to between 0.25 to 0.80 percent Mn, producing a slag with 18 to 22.5 percent Fe, 24.1 to 31.1 percent Mn, 8.4 to 12.8 percent SiO_2, and 16 to 26.4 percent CaO. Scrap and limestone were used as coolants. Since these workers used a fluid slag requiring high temperatures, evaporation losses were 30 percent.

In the same session, E. Herzog reported on experiments at the Thysen Works in Hamborn. By adding about 15 percent of coolant in the form of roll scale, the temperature of the melt was lowered, and the evaporation loss was decreased appreciably. One-third of the coolant was added at the beginning and the rest during the blowing. The spiegel had a manganese content of 7 to 9 percent. The slag with a crumbly nature favorable for separation of the intermediate metal contained 40 to 49 percent Mn and 13 to 24 percent Fe (entrapped metal included). The manganese loss appeared lower on the basis of paler color of evolved gases. The metal product was duplexed in an open hearth.

9/ Sonnenchein, A., German Patent 310,552, Apr. 11, 1917. See Stahl u. Eisen, vol. 39, 1919, p. 1051.

10/ Joseph, T. L., Barrett, E. P., and Wood C. E., Experiments Demonstrate Method of Producing Artificial Manganese Ore: Trans. Am. Inst. Min. and Met. Eng., vol. 90, 1930, pp. 378-404; also Stahl u. Eisen, vol. 50, 1950, pp. 1002-3.

11/ Bading, W., Stahl und Eisen, vol. 66, 67, 1947, pp. 180-186; and Houdremont, E., Stahl u. Eisen, vol. 58, 1938, p. 1195.

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In later experiments in 1937 at Rheinhausen[12], about 2,000 tons of spiegel with 0.4 to 1.5 percent Si and 10 to 12 percent Mn were blown. The manganese slags containted 38 to 39 percent Mn and 17 to 20 percent Fe (entrapped metal included). Contrary to the first experiments at this plant, these melts were cooled with ore in a manner similar to that reported by Herzog. Loss through manganese evaporation still amounted to about 20 percent, and manganese recovery lay between 63 and 66 percent. The residual melt with 0.26 to 1.0 percent C and 1.5 to 1.7 percent Mn was used for duplexing in the open hearth.

Since the slags obtained by Bansen and Herzog from blowing spiegel had only two to four times as much Mn as Fe, Bansen tried later, as suggested in correspondence by Lofquist,[13] to enrich the ratio of Mn:Fe in the slag, using sulfides of manganese in a refining furnace at lower temperatures 1,350° to 1,410° C. Slags with 48 to 56 percent Mn, 5.7 to 6.7 percent Fe, 12 to 17 percent SiO_2, and 3 to 9 percent S were obtained by this procedure. The Mn:Fe ratio (9:10) was very favorable. The spiegel with 0.3 to 0.9 percent Si and 10.5 to 18.8 percent Mn was reduced to a Mn content of 2.4 to 2.8 percent. A great disadvantage of this working method is produced by the high sulfur content of the slag, since the sulfur must be roasted off before treatment in the blast furnace.

In connection with this work; Oelsen[14] determined the relation in laboratory melts between manganese and phosphorus content of pig iron and slag and showed that, by substitution of silica for the sulfur, thin-fluid slags with good Mn:Fe ratio could be obtained at low temperatures. Nevertheless, although it replaces the troublesome sulfur, silica is harmful to manganese yield in the blast furnace.

During the war, spiegel was blown on a larger scale at several plants. W. Bading[15] reported on the results in various plants, in particular the August-Thyssen Co. in Hamborn and the Mannesman-Tube Co. in Huckingen. From the individual tests on blowing spiegel, this writer gives a series of compiled tables on phosphorus-spiegel production in the blast furnace and blowing in the converter, with manganese analysis of product and manganese losses. The different Mn and P content of slags at the various plants was analyzed by Bading according to varying temperature and slag condition.

Therefore, the aim of this work was to study the metallurgical principles of blowing spiegel and draw conclusions from them. The over-all influence of temperature and slag condition on the Mn:Fe and the Mn:P

12/ Bansen, H., Session of United German Engineers of Aug. 3, 1937; and Houdremont, E., Stahl u. Eisen, vol. 58, 1938, p. 1195.

13/ Benedicks, C., and Lofquist, H., Nonmetallic Inclusions in Iron and Steel: German Patent 652,278, London, 1930, pp. 110-111.

14/ Mitteilung Kaiser Wilhelm Institute für Eisenforschung, vol. 21, 1939, pp. 79-104; also,
Oelsen, Willy, Unterlagen zur Gewinnung manganreicher Schlacken aus Spiegeleisen und Phosphorspiegeleisen: Stahl u. Eisen, vol. 59, 1939, pp. 81-87.

15/ Work cited in footnote 11.

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ratios in the slag was given special attention. These two ratios are very important in the further use of manganese slags for ferromanganese production.

In the first melts, it was not possible to measure the temperature during blowing. However, the following tests were made to obtain preliminary operating information.

It was apparent, from previous experiments, that manganese and carbon do not always burn off equally strongly, but that, with change in temperature, a change in the oxidation sequence occurs.16/ From deliberations with Oelsen, the following effects of melt temperature were calculated.

On the reaction equation, C + MnO = Mn + CO, the equilibrium constant, K, is calculated as,

$$K = \frac{[C] \cdot (MnO)}{[Mn] \cdot CO},$$

or, since P_{CO} is taken as a constant, $K = \frac{[C] \cdot (MnO)}{[Mn]}$.

This $(K_{C.MnO})$ value was not easily measured in the converter; however, with the help of other equilibrium constants, the $(K_{C.MnO})$ value and its variation with temperature can be calculated. These calculations are shown in table 1.

At 1,400° C., for acid slags, the calculated value amounts to 76; at 1,700° C., only about 5. The value of $K = \frac{[C] \cdot (Mn)}{[Mn]}$ should accordingly, on the basis of its steep temperature coefficient, be a good measure of the melt temperature, if this proportionality is valid for the converter.

TABLE 1. - Calculation of equations

The calculation of equilibrium product $\frac{[C] \cdot (MnO)}{[Mn]}$ is obtained as follows:

(1) $K_1 = \frac{[O] \cdot 100}{(FeO)}$. (2) $K_2 = [C] \cdot [C]$ and (3) $K_3 = \frac{(MnO)100}{(FeO)[Mn]}$.

These combine as follows:

$$\frac{K_2 \cdot K_3}{K_1} = \frac{[C] \cdot (MnO)}{[Mn]} = \log K_2 + \log K_3 - \log K_1.$$

Equations for Suboxide Slags

(1) $\log K_1 = \frac{[O] \cdot 100}{(FeO)} = \frac{-4260}{T} + 1.790.$

16/ Müller, F. C. G., Zeitschrift Verein deutscher Ingenieure, 1878, p. 305.

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(2) $\log K_2 = [C] \cdot [O] = \frac{-790}{T} - 2.182.$

(3) $\log K_3 = \frac{(MnO).100}{(FeO).[Mn]} = \frac{+6234}{T} - 1.026.$

$$\log K_2 + \log K_3 - \log K_1 = \frac{-790}{T} - 2.182 + \frac{6234}{T} - 1.026 + \frac{4260}{T} - 1.790,$$

$$= \log K_{C.MnO} = \frac{+9704}{T} - 4.998 \text{ (for suboxide slags).}$$

Suboxide slags

T., °C.	T., °abs.	$\frac{9704}{T}$	-4.998	$K_{C.MnO}$	$K_{C.(Mn)}$
1,400	1,673	5.82	+0.82	6.6	5.1
1,500	1,773	5.48	+ .48	3.1	2.5
1,600	1,873	5.19	+ .19	1.5	1.2
1,700	1,973	4.93	- .07	.85	.66

Equations for silicate slags

$$\log K_1 = \frac{[O].100}{(FeO)} = \frac{-6080}{T} + 2.56,$$

$$\log K_2 = [C] \cdot [O] = \frac{-790}{T} - 2.182,$$

$$\log K_3 = \frac{(MnO).100}{(FeO)\,[Mn]} = \frac{+7940}{T} - 1.172,$$

$$\log K_2 + \log K_3 - \log K_1 = \log K_{C.MnO} = \frac{+13220}{T} - 5.91.$$

Silicate slags

T., °C.	T., °abs.	$\frac{13220}{T}$	-5.91	$K_{C.MnO}$	$K_{C.(Mn)}$
1,400	1,673	7.90	+1.99	97.5	75.8
1,500	1,773	7.46	+1.5	35.5	27.5
1,600	1,873	7.06	+1.15	14.1	10.9
1,700	1,973	6.70	+ .79	6.2	4.8

From these calculated values of the equation $\frac{[C].(Mn)}{[Mn]}$ the desired mass-action relationship of carbon and manganese in the metal can be determined for various melt temperatures. For 45 percent Mn in the slag

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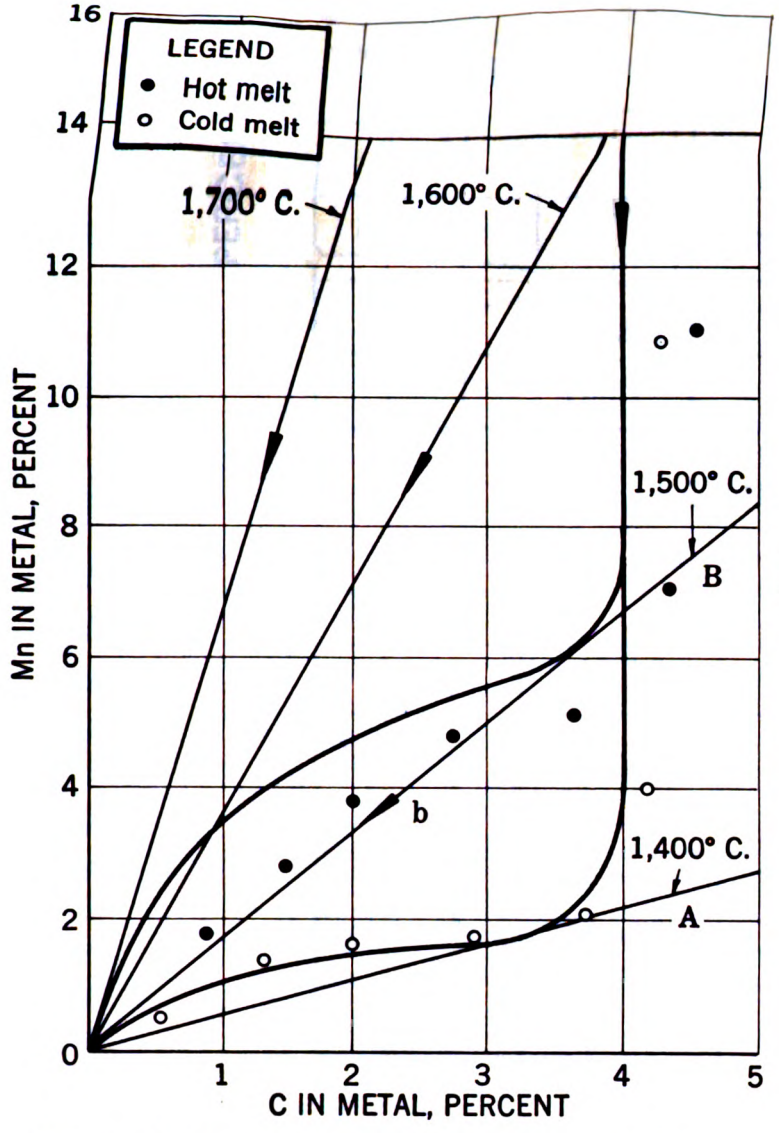

Figure 1. - Oxidation sequence of Mn and C at different melt temperatures.

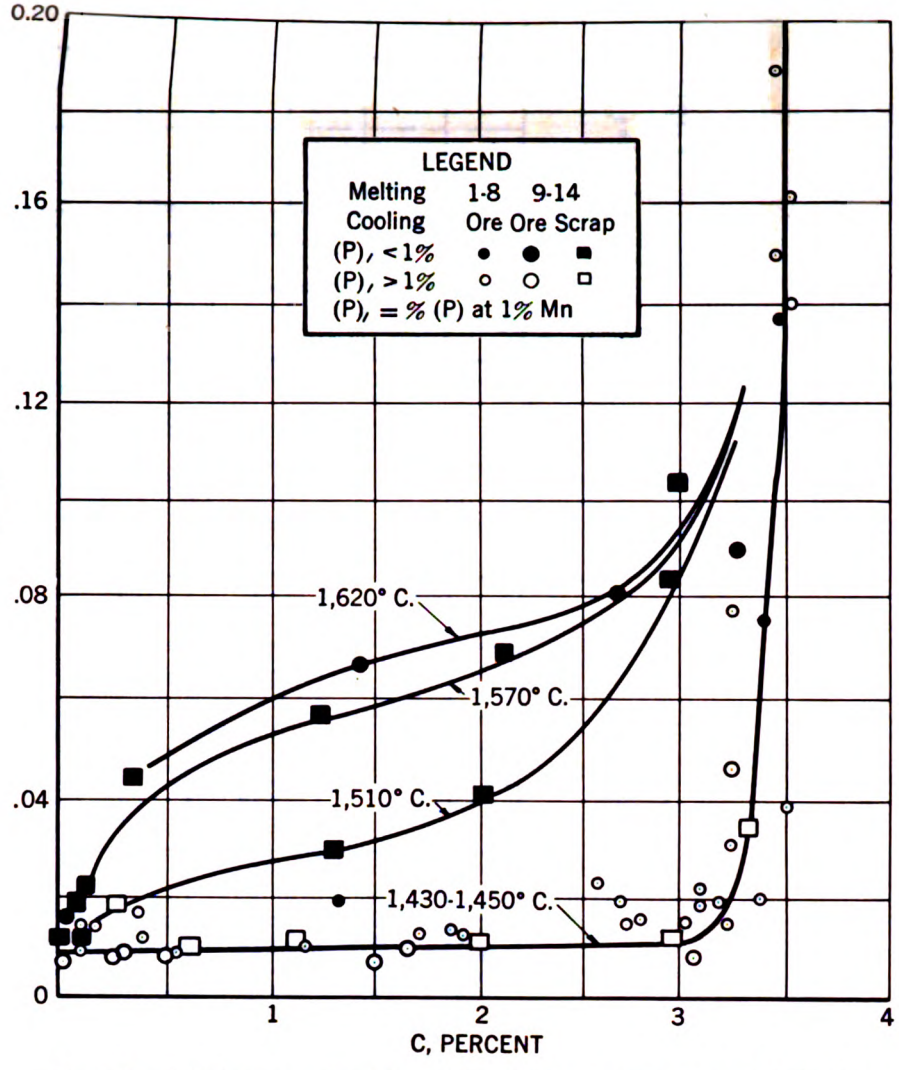

Figure 2. - Oxidation sequence of Mn and C in different temperature-controlled melts.

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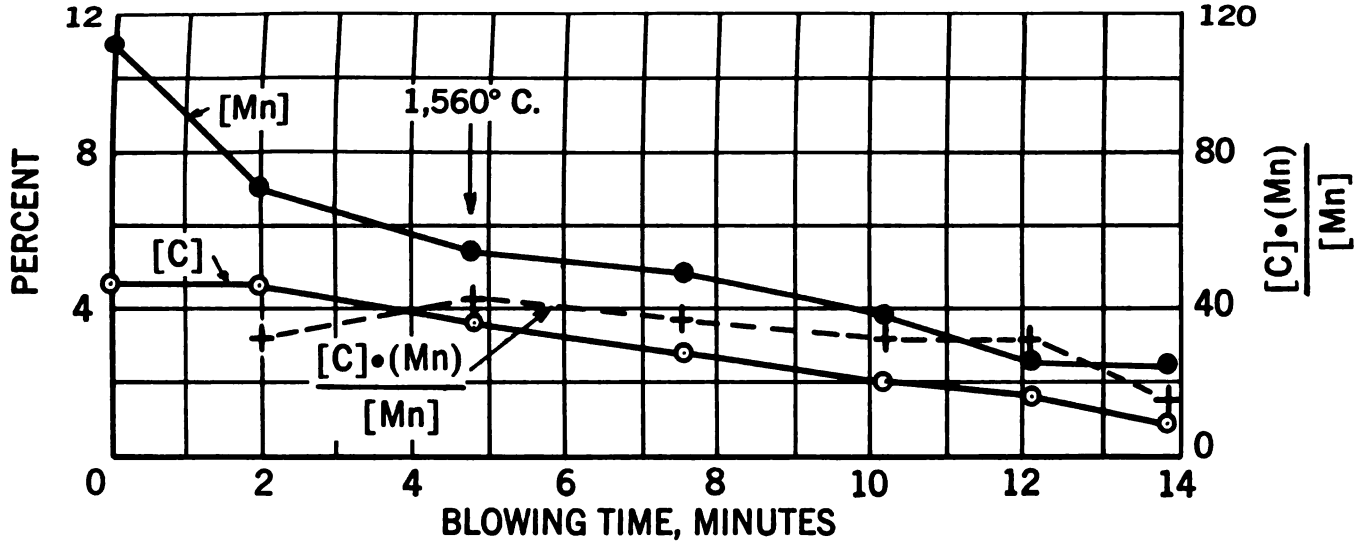

Figure 3. - Concentration changes of C and Mn in a hot melt.

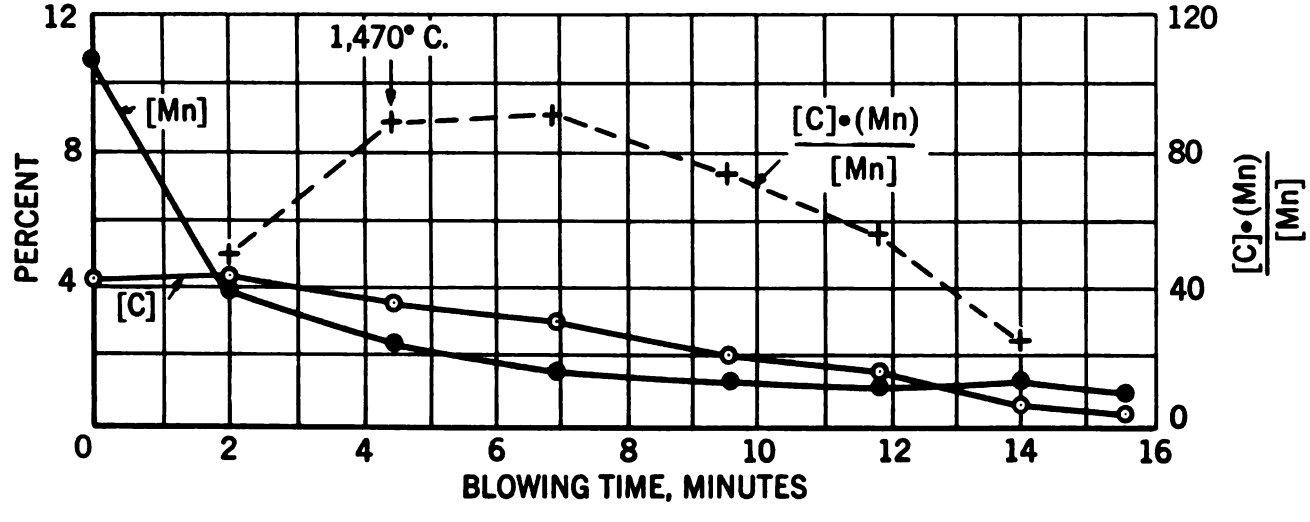

Figure 4. - Concentration changes of C and Mn in a cold melt.

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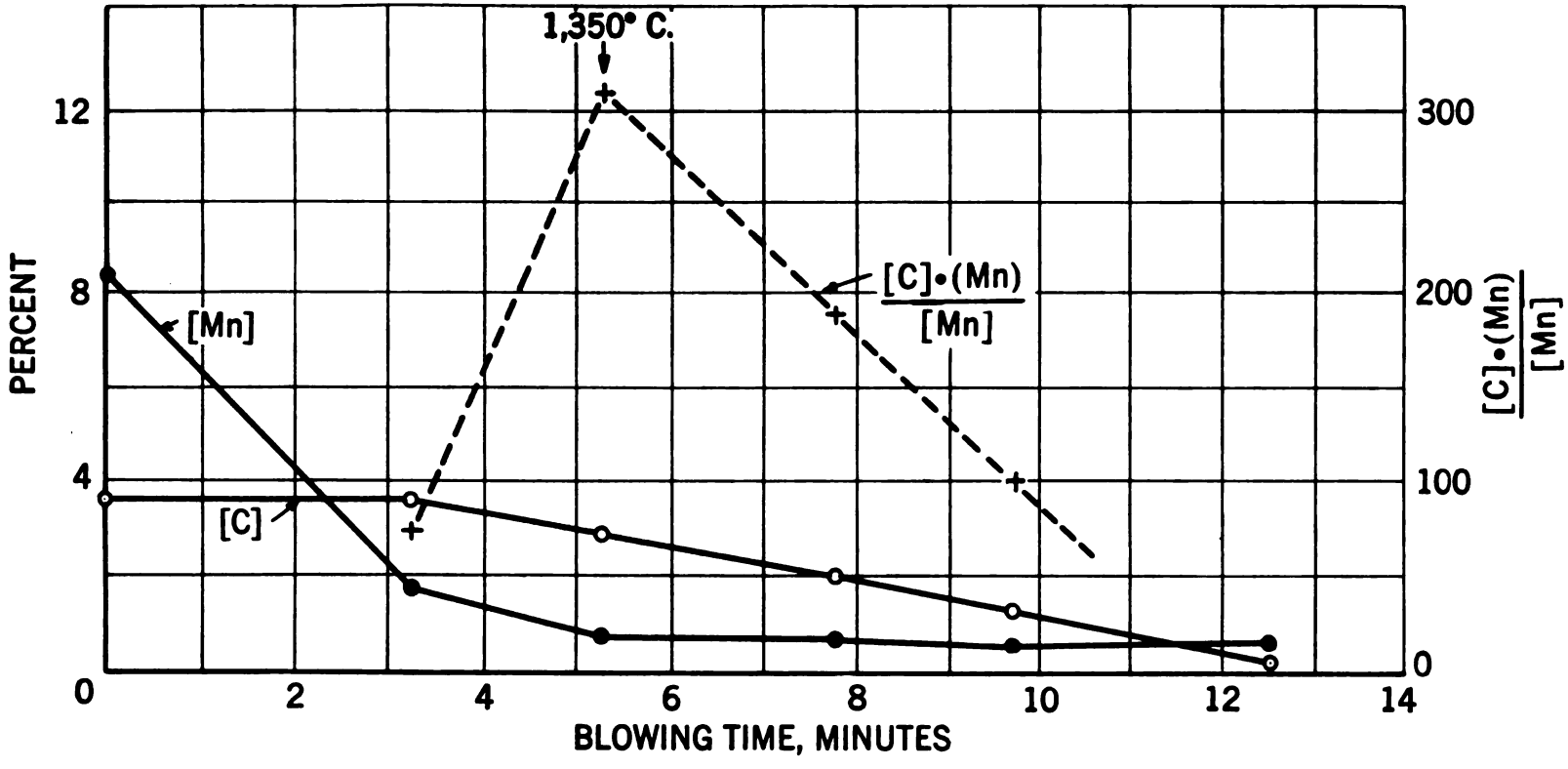

Figure 5. - Concentration changes of C and Mn in a very cold melt.

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at 1,400° C., $\frac{[C]}{(Mn)} = \frac{76}{45} = 1.7$. This means that, at this temperature, manganese alone oxidizes, until the proportion between C and Mn becomes 1.7. Accordingly, at 4 percent C in spiegel and about 12 percent Mn, the manganese alone should oxidize to 2.3 percent. Only then should the carbon begin to oxidize and continue to oxidize together with manganese (fig. 1, point A). Then, if the temperature of the melt stays the same, the concentration change of both elements goes along the line A (isotherm for 1,400° C.). Since th temperature rises because of further C and Mn oxidation, the concentration change follows the heavy crooked line. The final temperature of the melt on the figure is taken as 1,500°. The curve BO shows the concentration change for the temperature range of 1,500° to 1,700°. The analytical results of a hot- and cold-operated melt are plotted in figure 1. They follow the theoretical points well. However, the calculated curves do not show the true conditions entirely, since the manganese content of the slag is taken to be constant. However, it must depend on the manganese concentration of the quotient $(Mn)/[Mn]$.

The equation $\frac{[C].(Mn)}{[Mn]}$ rises during the melt until the carbon oxidizes, since until this time only the manganese content of the metal changes. After the oxidation of the carbon, the equation product drops appreciably.

The maximum of the equation product occurs, therefore, at a very definite temperature, namely the oxidation point of carbon.

These observations could be confirmed, since on later melts the temperature was measured by the method of G. Gille and J. Willems.[17] In figure 2, the mass action relationship of carbon and manganese for different controlled hot melts is plotted, beginning at a carbon content of 3.5 percent. In the cold-controlled melts of 1,430° to 1,450°, the manganese oxidizes first, nearly exclusively; and only at a very small values of $[Mn]/(Mn)$ does the oxidation of carbon set in. An essentially different path is followed by the melt at 1,620°. Carbon oxidation begins very early, and, consequently, Mn and C oxidize together.

Figures 3 to 5 show the reaction rates of three melts at different melt temperatures, to show the strong influence of temperature on the oxidation process. In the melt with the smallest cooling agent addition (fig. 3), manganese only oxidizes first, but the oxidation of carbon begins at fairly high manganese content, and then the two elements oxidize together. In the colder-controlled melt, a larger part of the manganese is slagged before the carbon oxidation sets in (fig. 4), and this is especially evident in very cold controlled melts (fig. 5). Before the oxidation of carbon begins, the equation product $\frac{[C].(Mn)}{[Mn]}$ rises in proportion to the delay period and then drops again. Only beyond the maximum point can equilibrium be approached;

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[17] Gille, von Gerhard, and Willems, Jacob, Temperatur und Flammenmessung beim Windfrischverfahren: Stahl u. Eisen, vol. 69, 1949, pp. 759-762.

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then the reciprocal action between carbon and manganese begins. Below 0.3 percent C and 1.0 percent Mn the equation product cannot be determined exactly, since small analytical errors in this range can lead to erroneous conclusions on the effect of temperature. The melt temperature can be measured on a number of melts during the oxidation, allowing the temperature coefficient of the $K_{C.(Mn)}$ product to be determined (fig. 6).

At around 1,550° to 1,700°, the equation product for pasty-crumbly and fluid slags agrees well with the theoretical value for silica-saturated slags; at lower temperatures, however, strong variation between the value for pasty-crumbly slags and the theoretical calculated value for silica-saturated slags appears. On the other hand, the value for fluid slags agrees also at the lower temperatures. Equilibrium methods fail, especially for pasty slags. Under fluid lime-bearing slags the product is much smaller, so that the calculated equilibrium for suboxide slags is very nearly approached.

A similar relation to that between [C] and (Mn) also should be expected between [C] and (Fe) (fig. 7). The product [C].(Fe) for [Fe] = 100 percent become smaller with rising temperature. The experimental data show this with appreciable scatter. These data however, lie for the silica-saturated, pasty-crumbly slags, considerably above the calculated values for silica-saturated slags. The iron content in the converter appears too high, so that the first oxidation product or the added ore in pasty-crumbly slags must be only partly reduced.

Whereas the $K_{C.Mn}$ value, accordingly, can be employed in spite of deviations from the calculated Isochore as an approximate measure of temperature, this is not possible with the [C].(Fe) product because of the larger scatter.

Another reaction constant that results from the slagging of iron and manganese is the K_{Mn} value. The amount of K_{Mn} value should be proportional to the melt temperature and the basicity of the slag. The relation of K_{Mn} value to temperature and basicity conforms to figure 8. The values for silica-bearing doughy slags lie between the values given by Korber and Oelsen[18] for silica-saturated and suboxide slags. High lime-content slags lie near the equilibrium curve for suboxide slags.

Since the temperature of the melt during the refining rises steadily, the K_{Mn} value during the process should decline to agree with the equilibrium of the process. This requirement however, is obtained first with less than 1 percent Mn in the metal. At higher Mn contents, the K_{Mn} values rise during the smelting process. This means that at higher Mn content a greater variation from equilibrium prevails. The iron content of the slags lies too high and the Mn:Fe ratio too low (fig. 9). These unfavorable iron contents are largely limited by the slag condition, with the slag condition at high manganese contents largely limited by the content of silica and lime. The higher

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18/ Mitteilungen aus den Kaiser Wilhelm-Institut für Eisenforschung, vol. 14, 1932, p. 181.
Korber, Friedrich, Untersuchunger über das Verhalten des Mangans bei der Stahlerzeugung: Stahl u. Eisen, vol., 52, 1932, pp. 133-144.
Mitteilunger aus den Kaiser Wilhelm Institut für Eisenforschung, vol. 15, 1933, p. 281.

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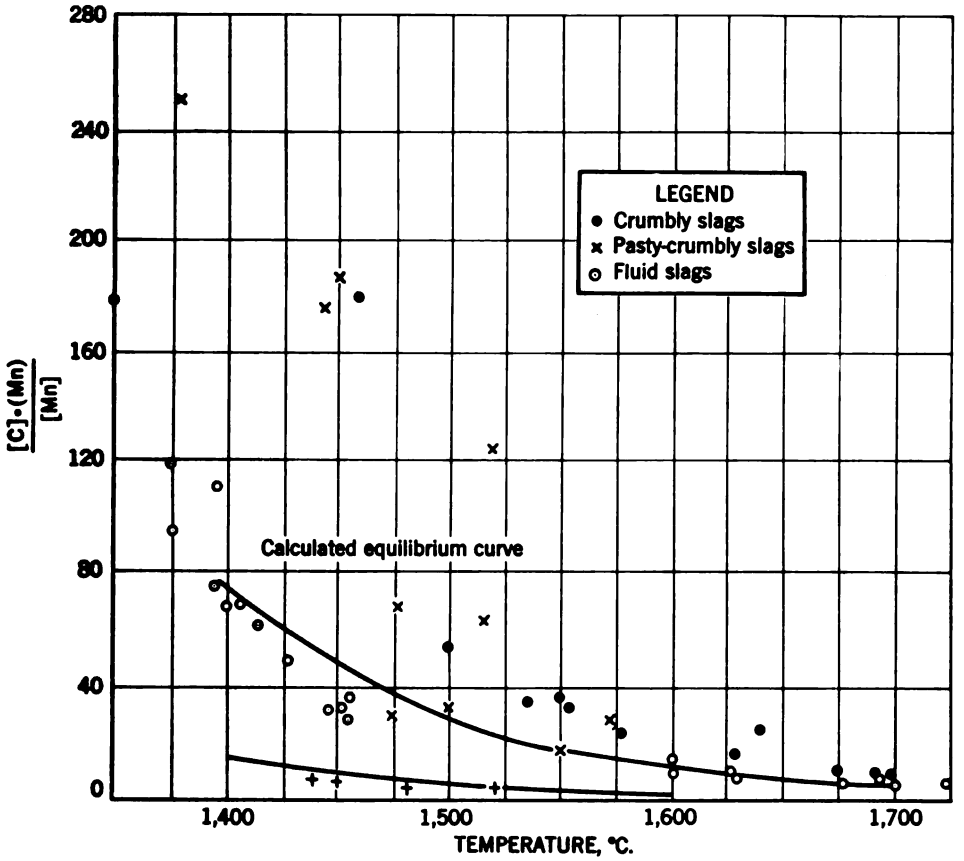

Figure 6. - Variation with temperature of factor $\frac{[C].(Mn)}{[Mn]}$.

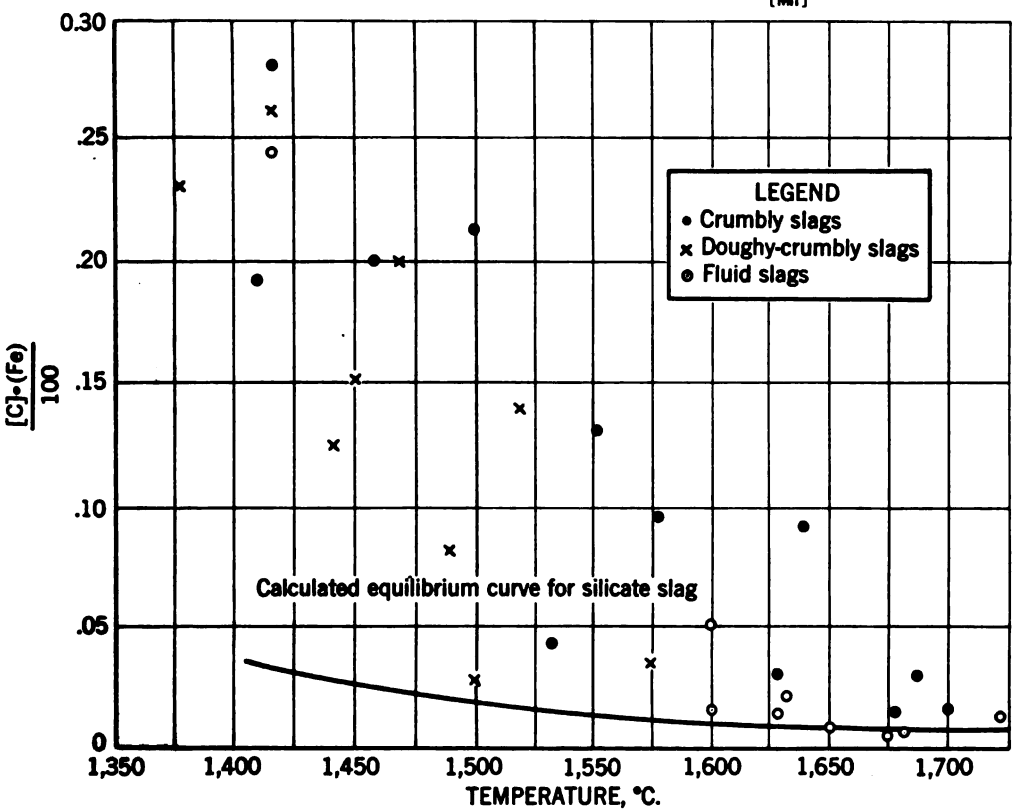

Figure 7. - Variation with temperature of the factor [C].(Fe).

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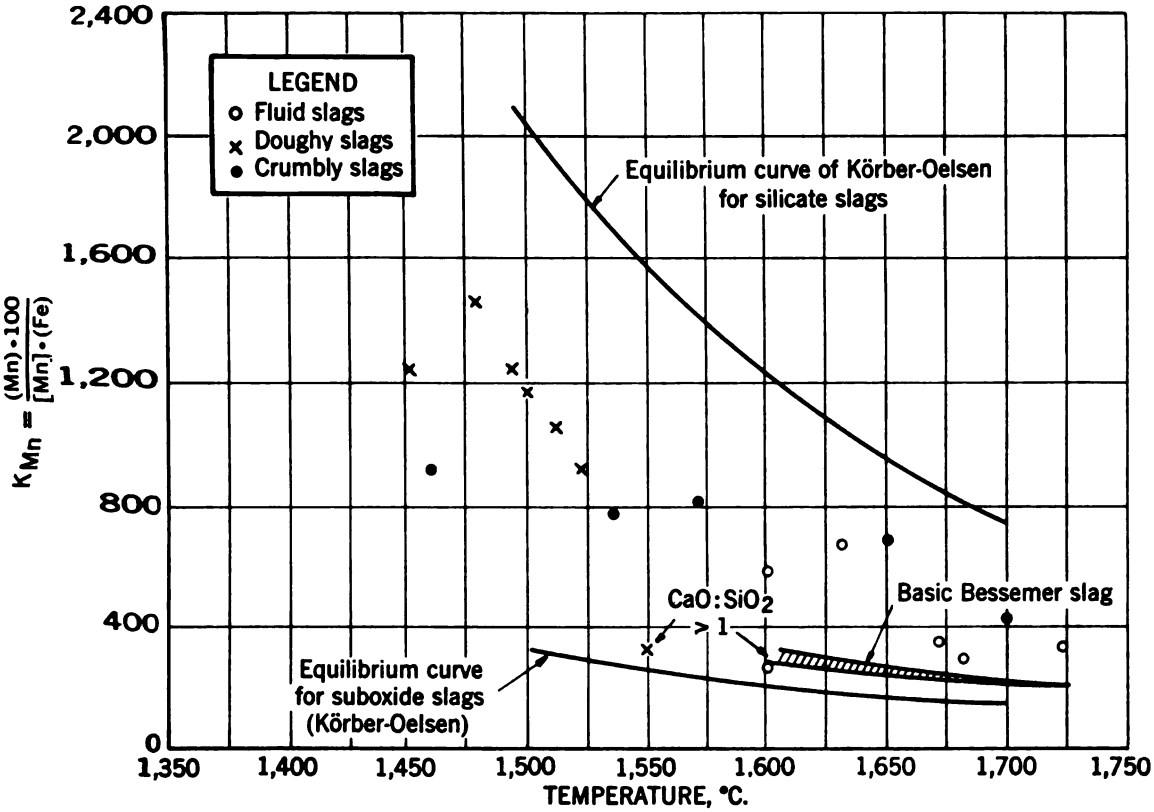

Figure 8. - Variation with temperature of manganese equilibrium product.

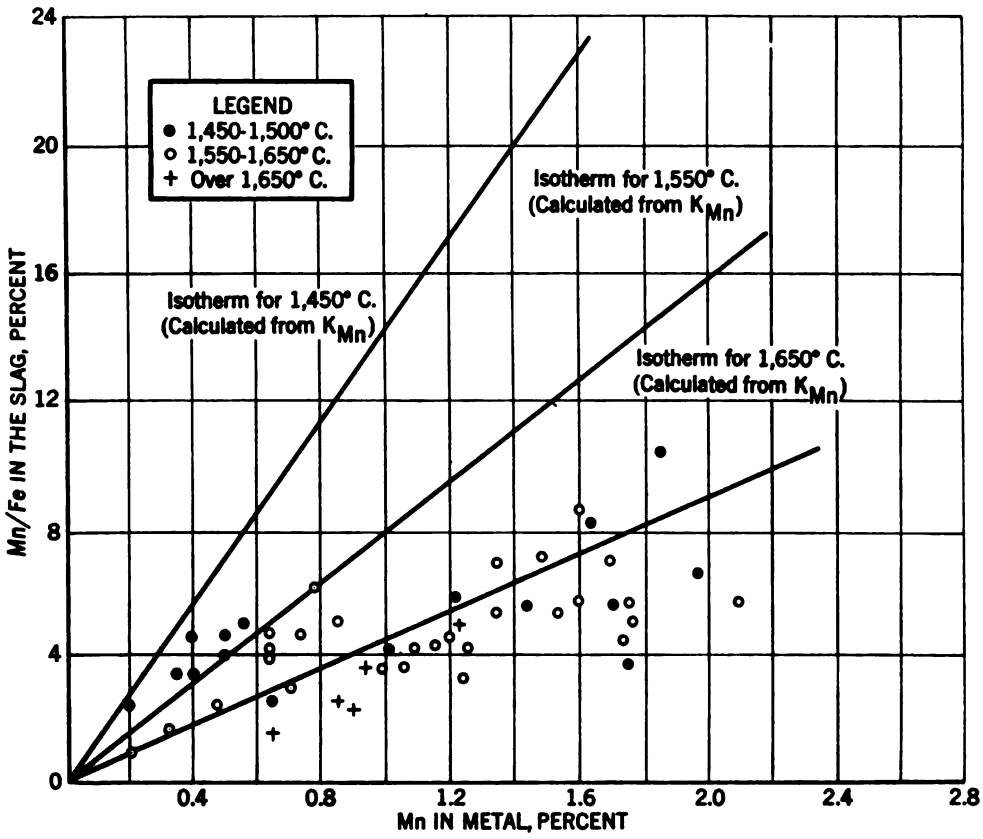

Figure 9. - Mn:Fe ratio in slags for various manganese contents in the metal.

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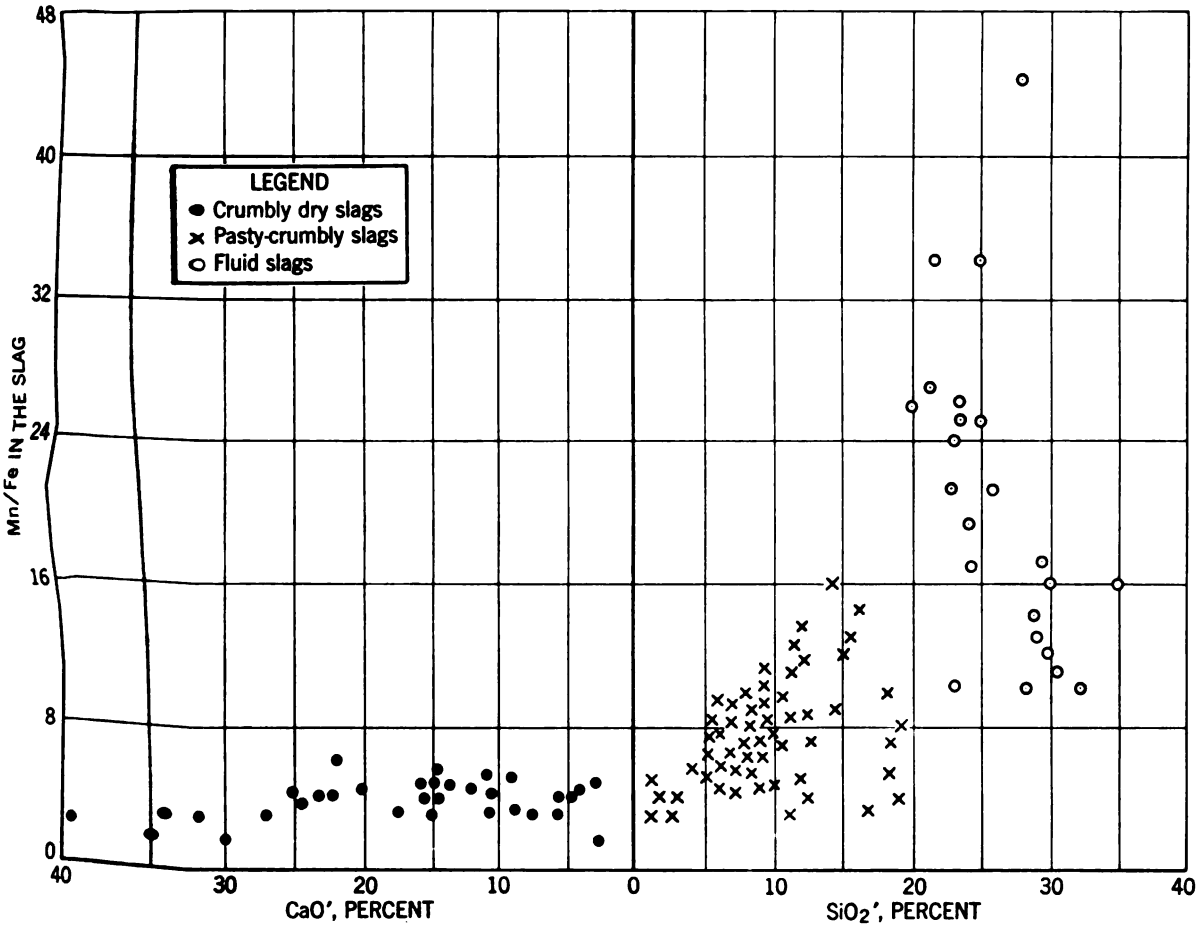

Figure 10. - Relationship of Mn:Fe ratio with slag composition and basicity.

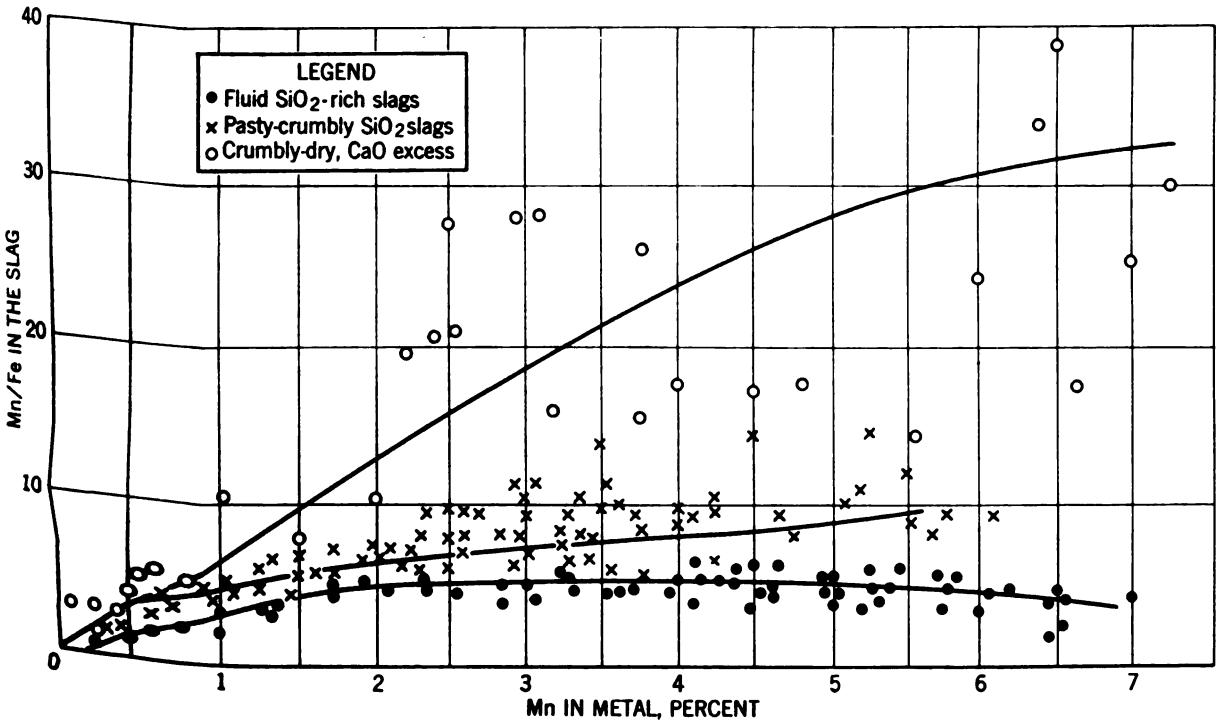

Figure 11. - Mn:Fe ratio in relation to manganese content of metal and slag composition.

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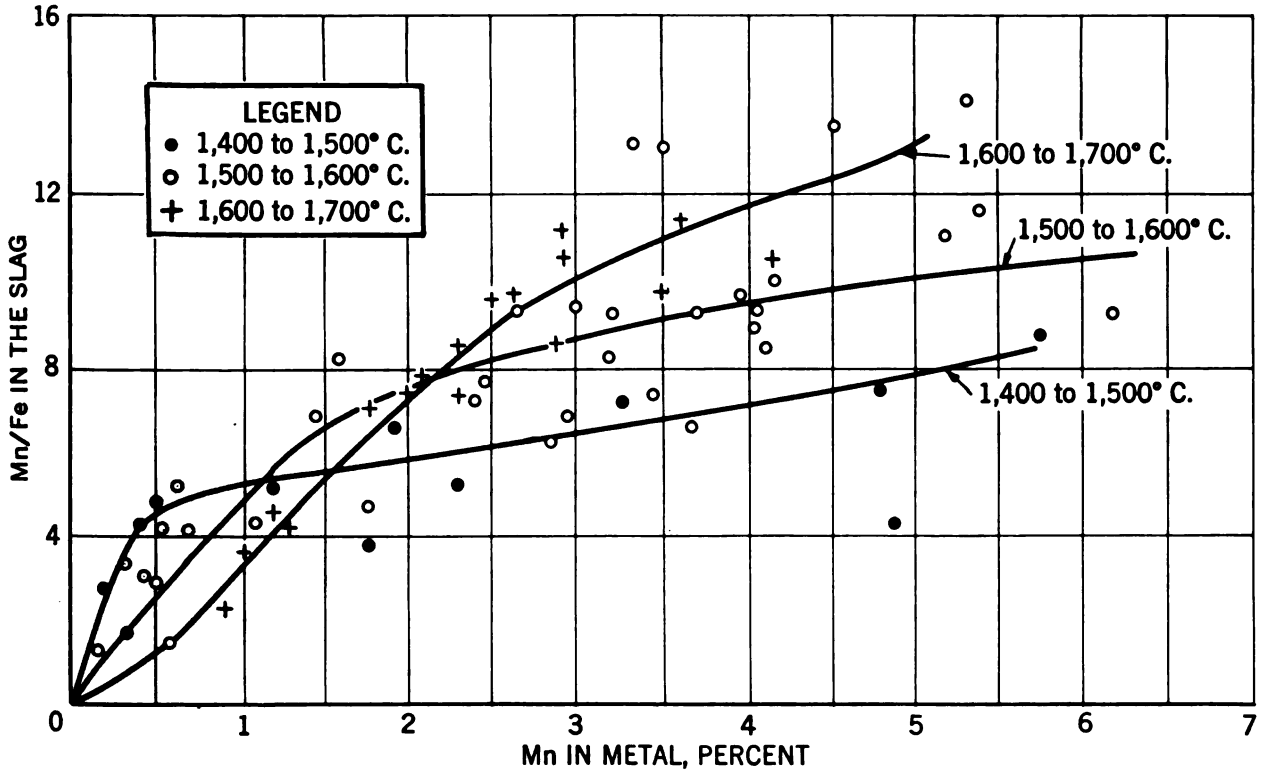

Figure 12. - Relationship of Mn:Fe ratio to temperature and manganese content in pasty-silicate slags.

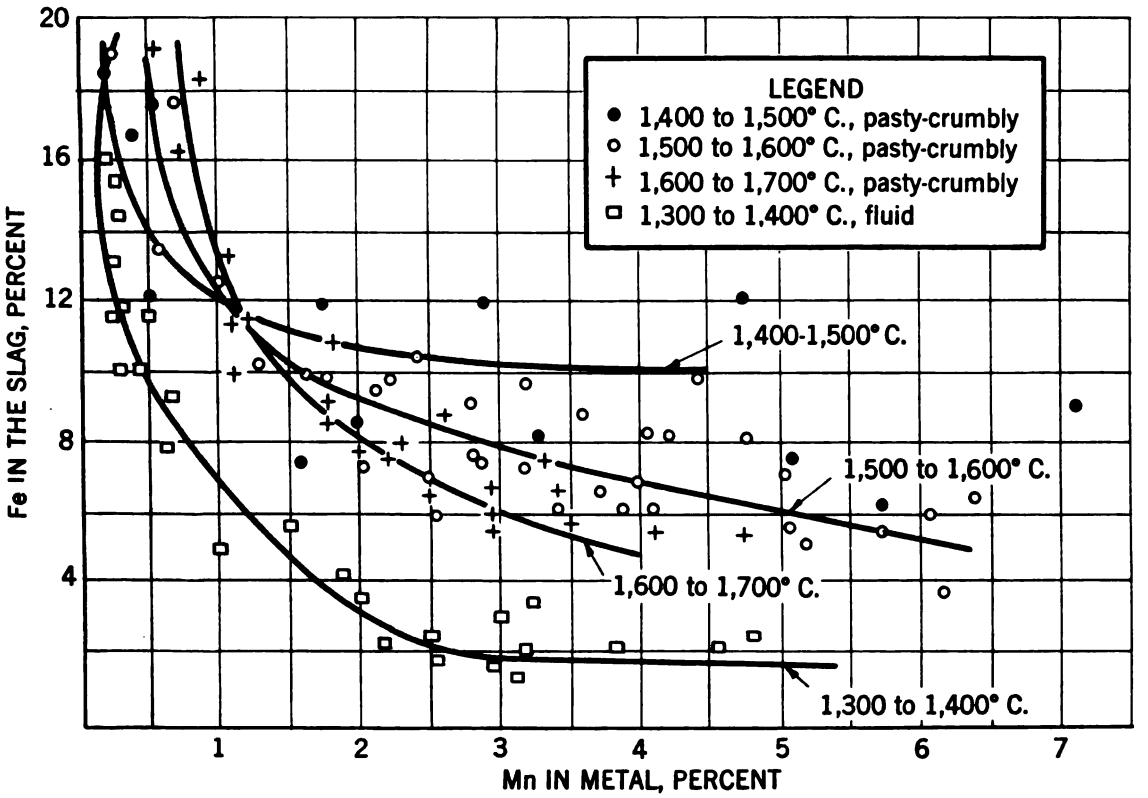

Figure 13. - Iron content of melts at different temperature and manganese content of metal for pasty-crumbly and fluid slags.

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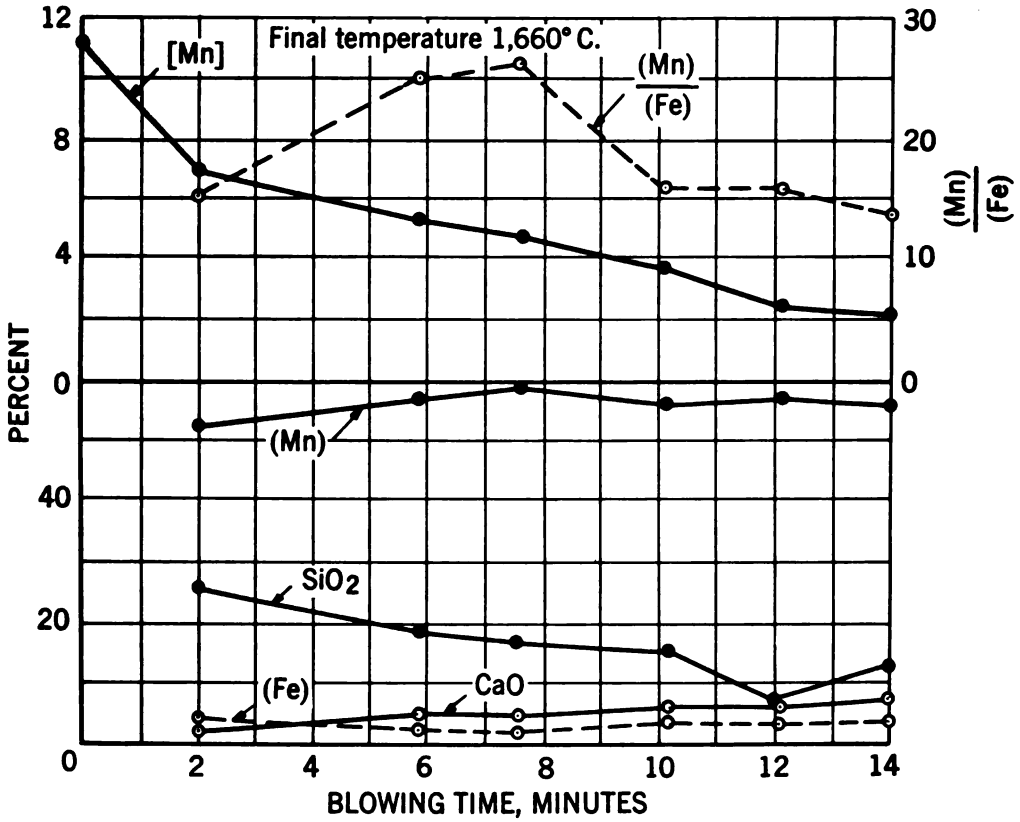

Figure 14. - Mn and Fe slagging in hot melt.

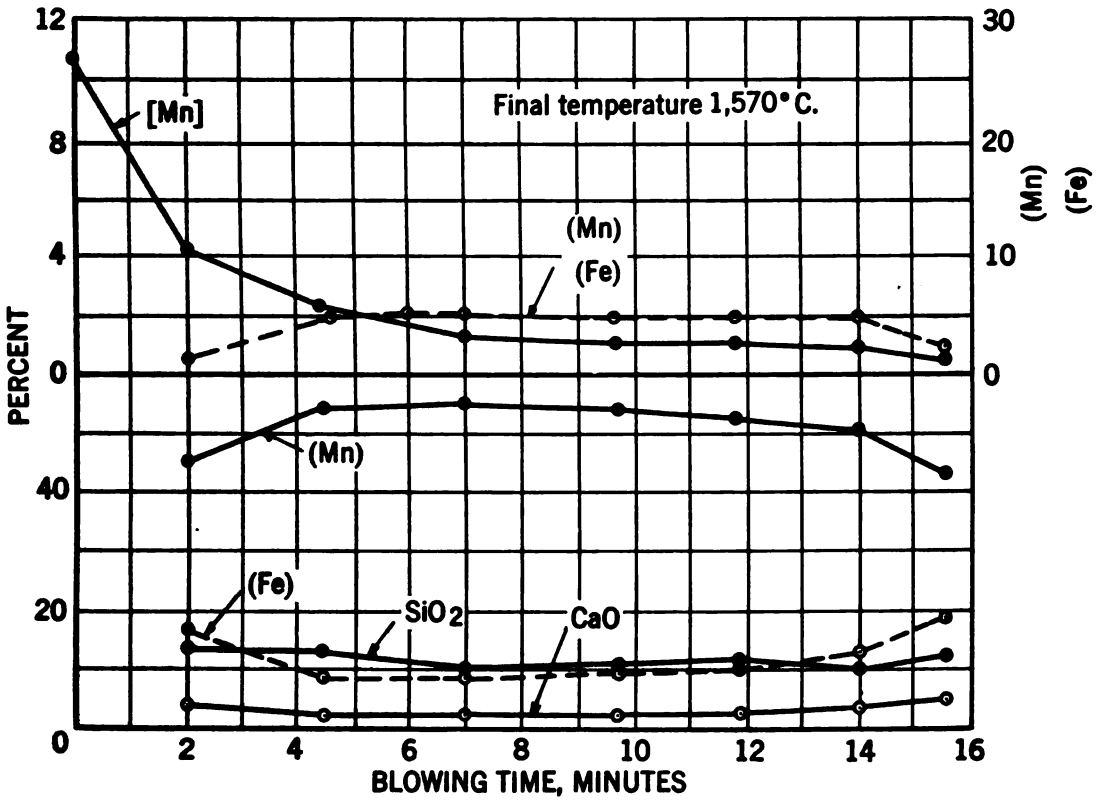

Figure 15. - Mn and Fe slagging in cold melt.

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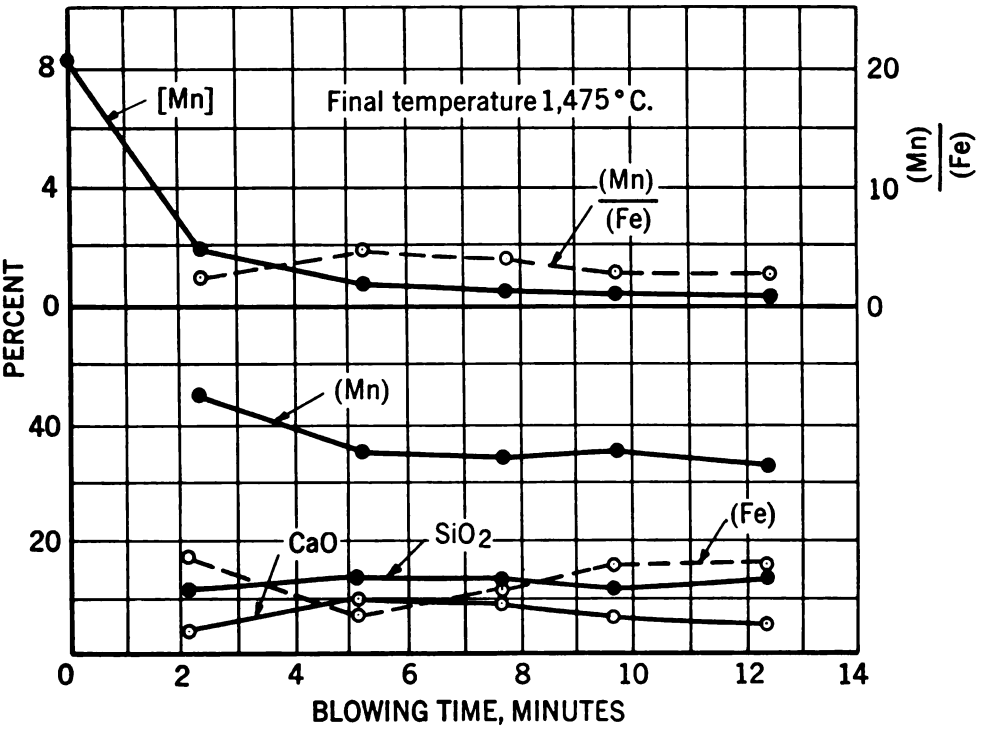

Figure 16. - Mn and Fe slagging in a very cold melt with doughy-crumbly slags.

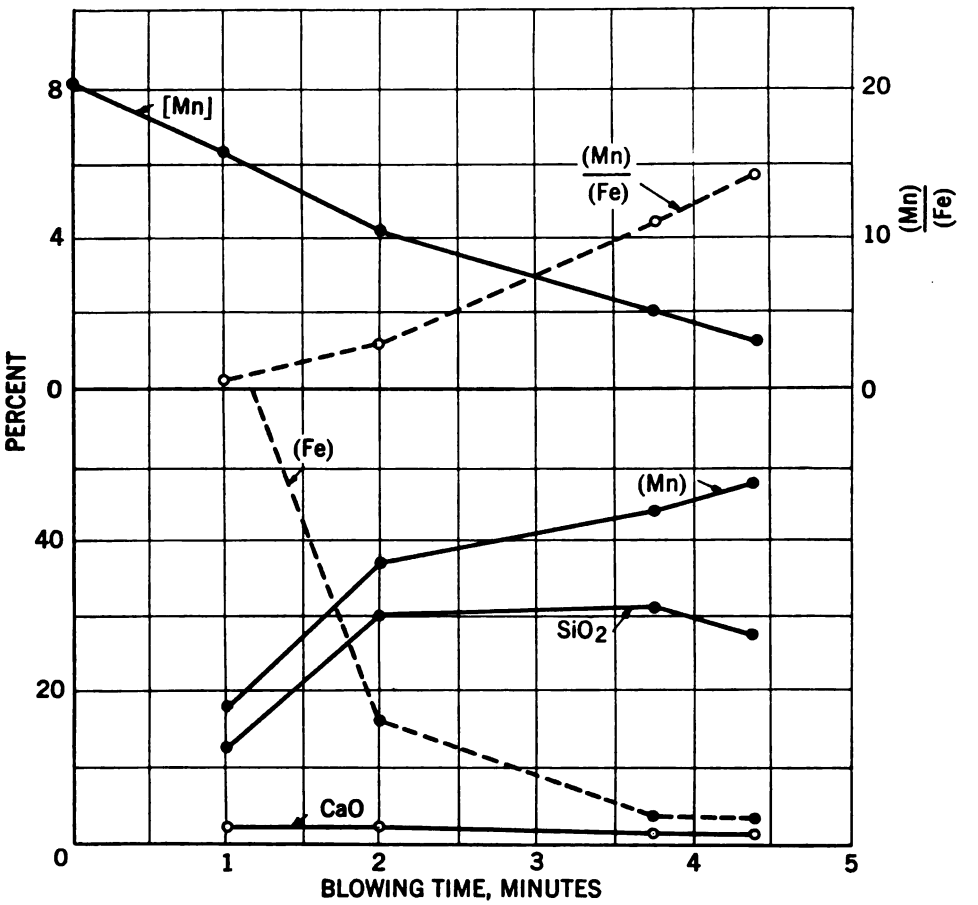

Figure 17. - Fe and Mn slagging in a melt very drastically cooled with ore having a fluid slag.

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the silica content of the slag, the more fluid it is and the better is the Mn:Fe ratio in the slag (fig. 10).

At the same slag composition, according to the investigation of W. Oelsen, a better (meaning higher) Mn:Fe ratio is to be expected for silica-rich slags than with oxide or basic slags. High basicity and crumbly slag permits only low ratios of Mn:Fe to be attained, while acid or fluid slags give appreciably better values (fig. 11). Under basic slags the best value of the Mn:Fe ratio is not likely to be over 5. Under 1 percent Mn a sharp drop of the ratio is to be expected because of the now strong iron-slagging action.

The influence of temperature upon the Mn and Fe slagging is twofold (fig. 12). At high Mn content, higher temperature affects the degree of fluidity of the slag and, at the same time, favors the reduction of a larger part of the FeO that is introduced by additions of ore or roll scale. This tends toward a favorable Mn:Fe ratio in the slag. At lower temperature, primary-formed (or from ore addition sources) FeO is reduced only partly, or not at all, since the FeO is prevented from reacting in further stages of the refining with solid MnO (solidification of slag at lower temperature and higher Mn content). At lower Mn contents (from 2 percent down), on the contrary, the higher temperature of the melt causes a rise in FeO content in the slag (fig. 13). This earlier increase in iron content at higher temperature is responsible for a strongly unfavorable effect on the Mn:Fe ratio toward the end of the blowing. The essentially later appearance of strong iron slagging at lower temperatures proceeds with lower Mn content of the metal to a more rapid fall in the Mn:Fe ratio. The plotted ratios hold, however, only for pasty slags or those that, in the course of the refining, are pasty or crumbly instead of for fluid slags. In the fluid slags the Fe contents, except through addition of ore, are very low and permit favorable Mn:Fe ratios.

The fact that, opposite to expectations, the melts at higher temperatures, with high manganese content, gave a more favorable Mn:Fe ratio than melts at lower temperatures, can be attributed definitely to the higher degree of fluidity of these slags and their better reducibility (assuming similar silica contents). (Figs. 14 to 17.)

As early as the second minute of blowing the hotter melts show an iron content of only 3.5 percent, in spite of additions of roll scale. The iron content remains low until the end and results in a favorable Mn:Fe ratio. The first-formed slag contains little CaO, but has a SiO_2 content of over 20 percent. The slag was fluid from the start and went gradually over into a doughy condition (fig. 14).

In the colder melts (figs. 15 and 16), the SiO_2 content was lower. Because of this lower SiO_2 content and lower temperature from the start the slag was only partly fluid. For this reason, the iron content was high from the start and did not drop below 10 percent during the blowing. Therefore, the Mn:Fe ratio was more favorable with the hot melt than by either cold one.

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In silica-rich fluid slags, even at lower temperatures, the iron content is decidedly lower in the slag and more favorable Mn:Fe ratios are attained (fig. 17). Although with large additions of oxide coolants the iron oxide was only slowly reduced, the slag showed a very high ratio of Mn:Fe at low manganese content in spite of the lower temperature of only 1,400° C. The slow lowering of the iron content of the slag at the beginning is caused by the slow solution of the ore additions.

Blowing of Phosphor-Spiegeleisen

By blowing phosphorus-rich pig iron, the same process of slagging of iron and manganese occurs as for low-phosphorus pig iron. However, because of the high phosphorus content of the crude iron, the danger persists, that the slag will absorb too high a content of P_2O_5 and no longer be useful for the preparation of low-phosphorus ferromanganese. Herzog19/ has commented on this difficulty. In 1937, Herzog blew a high-phosphorus spiegel and prepared a slag with 53 to 56 percent Mn and 0.23 to 0.38 percent P (not including entrapped metal). The metal could not be blown under 1.2 to 1.4 percent manganese and 0.11 percent C, otherwise the phosphorus content of the slag would rise rapidly. Herzog found a neutral lining favorable to blow phosphorus-bearing spiegel.

During the war, the August Thyssen Works blew over 3,000 tons of phosphorus-iron. The metallurgical data were reported by Eichholz, Kootz, and Oelsen.20/

Bading, in his comprehensive publication,21/ reported on the technical operational results of this and his own researches. Later the August Thyssen Works research on high-phosphorus iron at lower temperatures and under fluid slags was carried out.22/

The evaluation of the complete process on high-phosphorus spiegel irons indicated that the phosphorus content of the slag was strongly influenced by both the manganese content of the intermediate metal and the melt temperature (fig. 18). Lower melt temperatures cause higher phosphorus content of the slag at the same manganese content of the intermediate metal. A manganese content higher than 2 percent in the intermediate metal has no effect on the phosphorus content of the slag. On the other hand, a small change in manganese content of the intermediate metal below 1 percent causes a strong slagging of phosphorus. The slag condition (pasty-crumbly or fluid) has the following effect: Fluid slags at the same temperature had lower phosphorus content than pasty or crumbly slags. An effect of converter lining (magnesite, Mangal, dolomite) upon the phosphorus slagging was not detected in this research. The use of scrap or ore as a cooling agent had no apparent

19/ Unpublished. (See Oelsen, W., Unterlagen zur Gewinnung manganreicher Schlacken aus Spiegeleisen und Phosphorspiegeleisen: Stahl u. Eisen, vol. 59, 1939, p. 84).

20/ Bading, W., Bericht Unterausschutz Thomasbetreib VDEH, article 3, June 3, 1942, p. 183.

21/ See footnote 11.

22/ Willems, J., and Hofges, H., Report of Metallurgical Division of August Thyssen Works: 1944 (unpub.).

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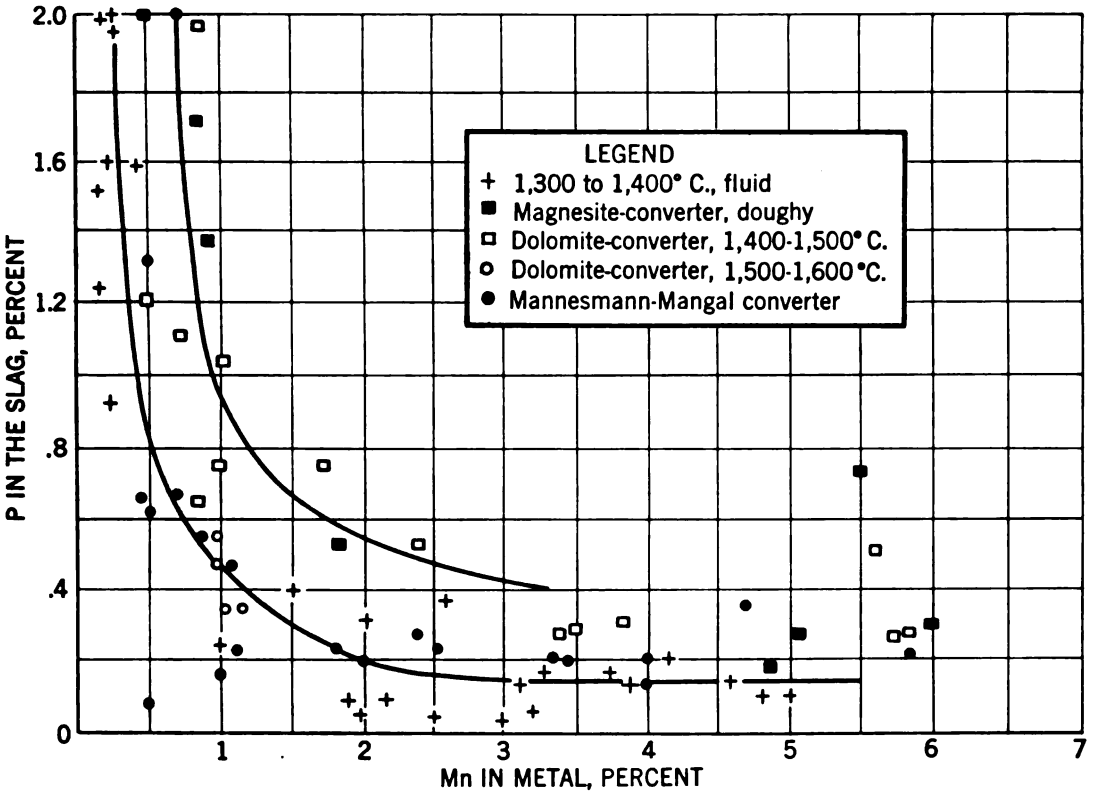

Figure 18. - Phosphorus content of slags in relation to manganese content in metal at different temperatures and different slag compositions.

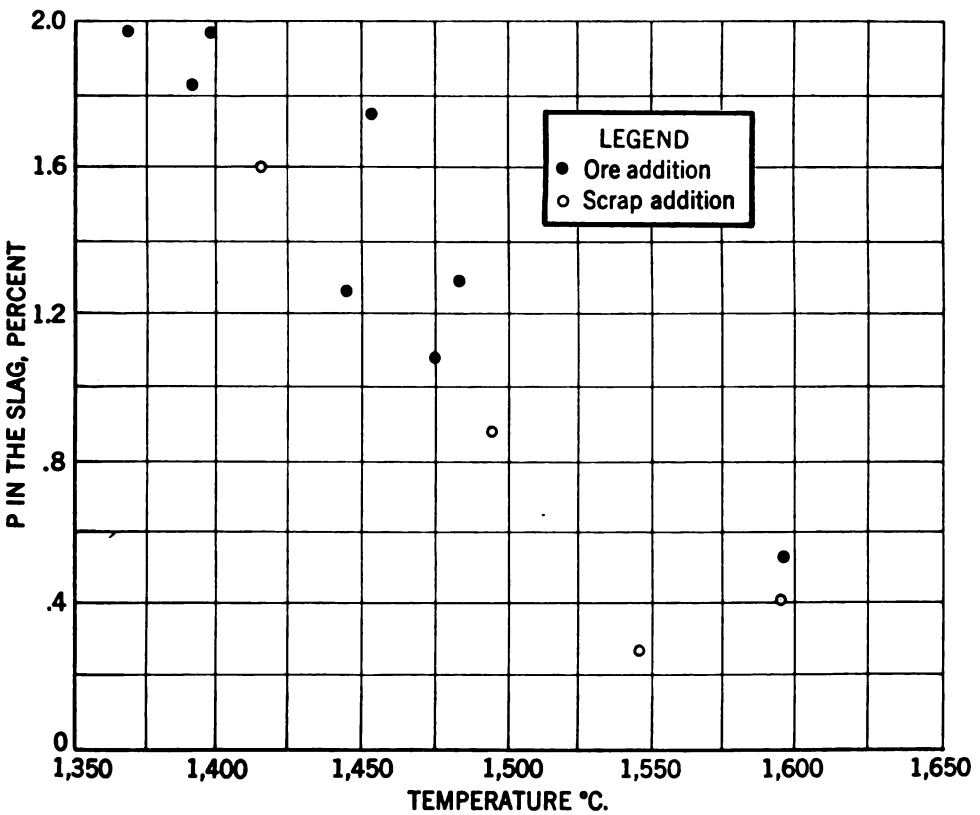

Figure 19. - Phosphorus content of slags at 1% [Mn] in metal in relation to temperature.

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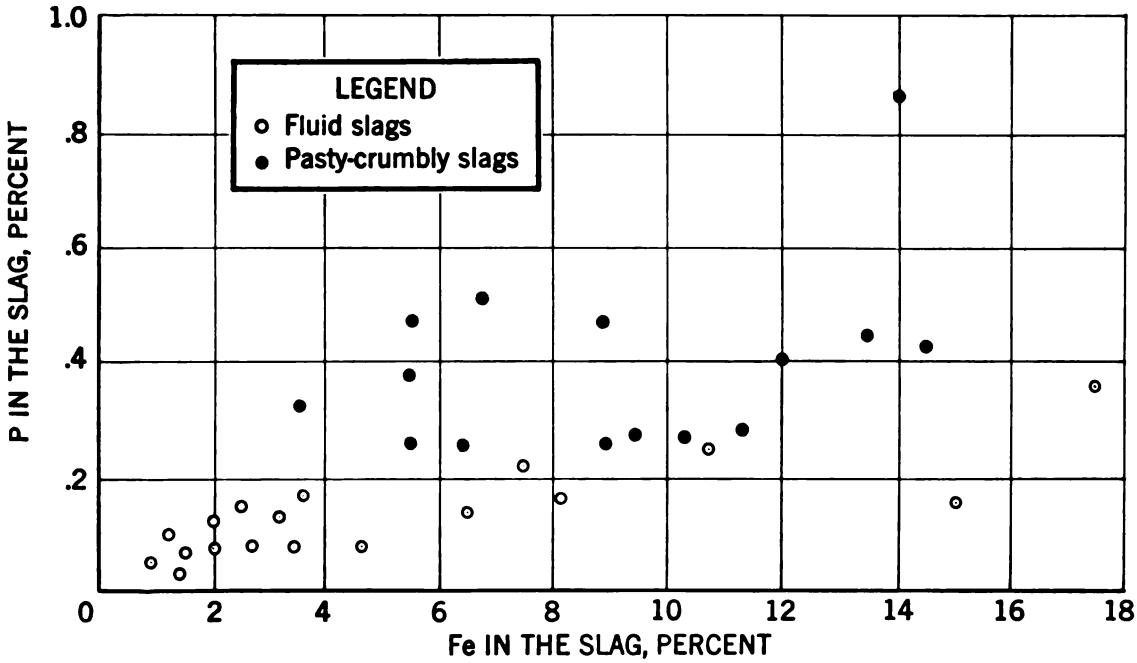

Figure 20. - Phosphorus content of slags in relation to iron content of the slag at 1.5 to 5% Mn in the metal.

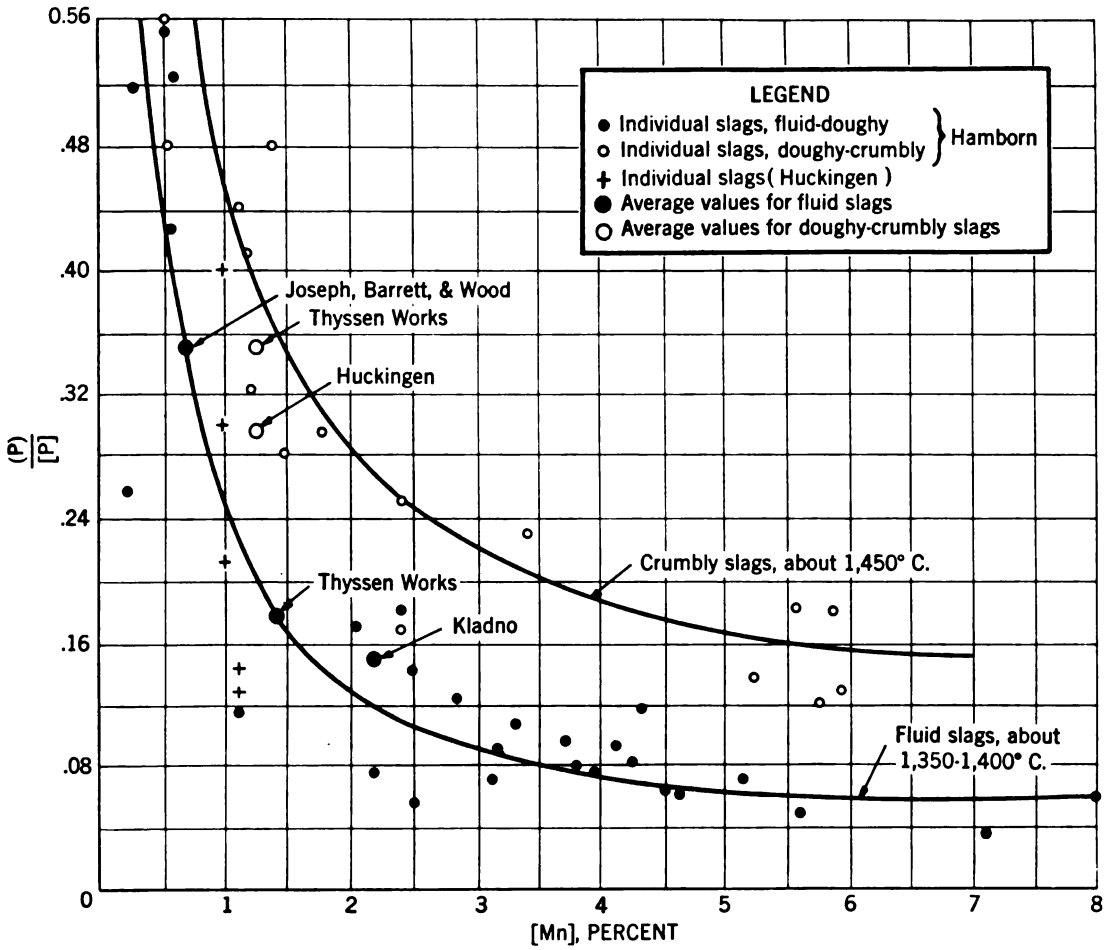

Figure 21. - Phosphorus slagging by blowing phosphorus-spiegel at various plants.

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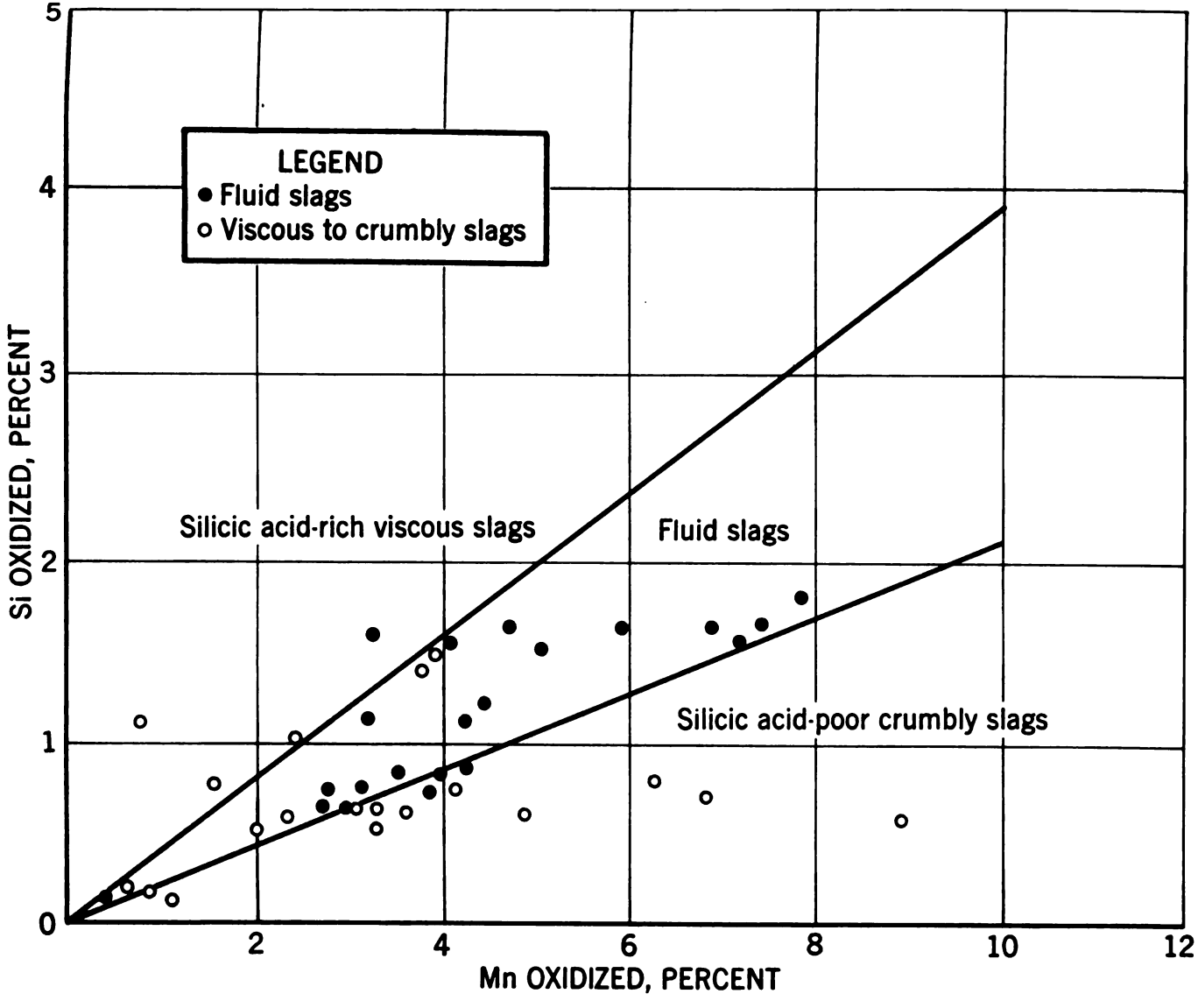

Figure 22. - Slag condition in relation to content of Mn and Si for temperatures from 1250°-1400° C.

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influence on the phosphorus content of the slag. The temperature dependence of the phosphorus slagging is great (fig. 19). Besides, a relationship exists between the iron and phosphorus content of the slag, which holds for fluid and probably for doughy-crumbly slags, that may be attributed to a chemical compound of iron and phosphorus (fig. 20).

Technical Results

Table 2 summarizes available data on blowing manganiferous pig iron.

Refining of hot metal for steel melting in the premixer or converter is based fundamentally on the same metallurgical laws as the blowing of spiegel. Accordingly, a manganese slag with good Mn:Fe ratio can be obtained only if no lime is added and the intermediate metal is not refined under 1 percent manganese. If the melt is finally blown to steel or duplex metal without slagging off, however, the resulting manganese slags are unsuited for preparing ferromanganese. They may, however, without additional manganese material, be charged into the blast furnace for Thomas or basic steel production.

Blowing phosphorus spiegel is not a difficult operation, since the intermediate metal produced, because of its phosphorus content, can be finish blown without additions to steel in a second converter, or it can be reduced in a mixer. The high-phosphorus intermediate metal thereby raises the manganese content of Thomas pig iron, whereas the silicon content is lowered. Compared to blowing low-phosphorus spiegel varieties, the phosphorus content of the metal makes a higher temperature reserve unnecessary.

To obtain the lowest phosphorus content in the slag, which is desired for the preparation of low-phosphorus varieties of ferromanganese, there are two possibilities. These are: Operating at a temperature of 1,350° to 1,450° C. with a fluid manganese silicate slag (proposed by Oelsen) or at temperatures of 1,550° to 1,650° C. with a pasty-crumbly manganous oxide slag. Comparison of these different methods of production is possible if the ratio of phosphorus in the slag and phosphorus in the metal to the manganese content of the intermediate metal is calculated. The most-favorable results can be attained with fluid or pasty-fluid slags (fig. 21).

Phosphorus spiegel was blown with fluid manganese silicate slags at low temperatures in Kladno with a crude iron with 6.7 percent Mn, 1.7 percent Si, and 3.6 percent to 4.2 percent P. In Hamborn, a spiegel was blown with 4.5 to 8 percent Mn, 0.7 to 1.7 percent Si, and 1.5 to 1.9 percent P.

By working with a fluid manganese slag, the proportion of Mn:Si in the pig iron must be held in the limits of 2.5 to 4.5, in order to reach the requisite silica content of 25 to 35 percent in the slag (fig. 22). If the silicon content of the pig iron is lower in order to obtain the required ratio, additions of silica-bearing cooling agents make a fluid slag obtainable. If the silicon content is too high, a slag of the desired composition is obtained by raising the manganese content in the pig iron.

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TABLE 2. - Technical data of blowing high-manganese pig iron

No.	Writer	Publication	Plant	Year	Blown quantity, tons	Crude metal analysis, percent				Intermediate metal, percent			Slag composition, percent						Application of metal	Temp. avg., °C.	Slag condition	Mn yield in slag	Ratio (Mn)/(Fe)	Mn evaporation
						C	Si	Mn	P	C	Mn	P	CaO	SiO_2	Mn	P	Fe comb.	Metal granules	Fe total					
1	E. Killing	Stahl u. Eisen vol. 47, 1927, pp. 1197-1203. Stahlw. Aussch. vol. 125.	Bochum	1927	Experimental	4.25	0.65	3.00	0.14	2.6-3.6	0.25-.50	0.018-.036	14-21	13-17	25-29	0.5-1.0	19-23	-	-	Duplex	-	Fluid	-	1.3	-
2	W. Eicholz, E. Herzog, Th. Kootz	Unpublished.	August-Thyssen-Hütte, Hamborn	1938	-	-	.5-.85	2.5 3.2	.10 .12	.05	.30-.55	.04-.07	33-36	15-16	20-26	.55-.65	12-14	-	-	Steel and duplex	-	do.	-	1.7 1.9	-
3	E. Herzog	do.	do.	1937	-	-	.20-.3	6.3-7.8	1.1-1.4	.11	1.2-2.4	-	6-8	7-10	53-56	.23-.38	6-10	Not anal.	-	-	-	Crumbly	-	-	-
4	W. Bading	Stahl u. Eisen vol. 66/67 1947, p. 180.	Mannesmann, Huckingen	1942	-	3.95	.45	6.54	2.2	-	1.3	-	3.3	13.1	42.0	.63	7.20	7.85	15.05	Steel	1,550	Pasty	-	3.5	-
5	W. Eicholz, Th. Kootz, W. Oelsen	Thomas-Aussch. VDEh June 3, 1942, s.a. Bading.	August-Thyssen-Hütte, Hamborn	1942	3,640	-	.2-.5	4.15	1.9-2.3	-	1.32	-	4-5	13-15	43	.7	6.0 7.5	8.0	14 15.5	Mixer and steel	1,400-1,500	do.	70	3.0 2.7	2
6	R. Zurek	Thomas-Aussch. VDEh June 3, 1942.	Kladno	1942	-	2.3	1.7	6.75	3.6-4.2	1.30-1.80	1.90-2.40	3.40 3.90	6.80	26.0	41.0	.55	2.5	3	5.5	-	-	Fluid	-	13.2	-
7	J. Willems, H. Hofges	Unpublished.	August-Thyssen-Hütte, Hamborn	1944	500	3.5-3.9	.7-1.7	4.5-8.0	1.5-1.9	3.3-3.5	1.1-1.5	1.4-1.95	2-7	31-34	36-43	.05 .15	2.5-4.5	3	4.5 7.5	**Mixer**	1,350-1,400	do.	-	8.0 5.8	Small
8	E. Herzog	Stahlw-Aussch. VDEh January 19 1937.	do.	1936	-	4.1-5.0	.4-1.4	7.40-11.0	.075-.135	(1.30) .2-1.9	(1.96) .5-2.5	-	7	11.80	49-47	.17	10.30	-	12.9 17.1	Duplex	1,530	Crumbly	-	3.8	Do.
9	H. Bansen, I. Wittig	do.	Krupp-Rheinhausen	1936	-	-	-	12-20	-	-	.28-.75	-	16.0 26.4	8.4-12.8	24-31	-	8-28.5	-	-	-	-	Pasty fluid	-	-	30
10	H. Bansen	Stahlw. Aussch. VDEh Aug. 3, 1937	do.	1937	1,300	-	1.0-1.5	10-11	-	.82-1.14	1.55	-	14.3	13.7	38	.14	16.7	11.8	28.5	Duplex	-	Pasty-crumbly	66.2	1.3	20
11	Do.	do.	do.	1937	600	-	.42-.68	10.5-11.3	-	.10 .53	1.01 2.75	-	13.5	8.7	39	.19	19.7	10.1	29.8	do.	1,660-1,720 est.	do.	63.7	1.3	22
12	W. Eicholz, Th. Kootz	Unpublished.	August-Thyssen-Hütte, Hamborn	1943	4,189	-	-	10.5	-	-	1.70	-	5.0	9.0	48	.05	9.2	13.5	22.7	Mixer	1,530	do.	74	2.1	11
13	W. Eicholz, Th. Kootz	do.	do.	1943	2,591	4.7	.59	10.0	.13	.67	2.05	.15	6.8	10.2	47	.05	8.5	12.5	21.0	Steel and duplex	1,640	do.	77	2.2	14
14 1/	W. Eicholz, Th. Kootz	s. W. Bading: Stahl u. Eisen vol. 66/67 1947, pp. 181-182.	do.	1943	-	-	-	-	-	-	-	-	8.0	11.0	53	-	6.0	.5	6.5	-	-	-	-	8.2	-
15	W. Eicholz, Th. Kootz	Unpublished.	do.	1943	3,983	-	-	9.75	-	-	1.79	-	5-10	10.0	45	.04	8.3	15.0	23.3	Steel and duplex	1,710	Crumbly	64	1.9	21
16	C. Wens	do.	Krupp-Rheinhausen	1943	5,061	4.4	.7	10.7	.13	.82	1.49	.145	10.7	-	42	.11	8.8	9.3	18.1	Duplex	-	Pasty-crumbly	-	2.3	-
17	T. L. Joseph E. P. Barrett, C. E. Wood	Stahl u. Eisen, vol. 50, 1930, pp. 1002-03.	Amerika	1930	Experimental	4.5	- -	12-15	.5	3.4	.75	.45	-	14-16	45-50	.15-.20	5.5-8 0	-	-	-	-	Fluid	-	8.2 6.3	-

1/ Manganese slags from experiment 13 after separation of metal granules with a magnetic separator.

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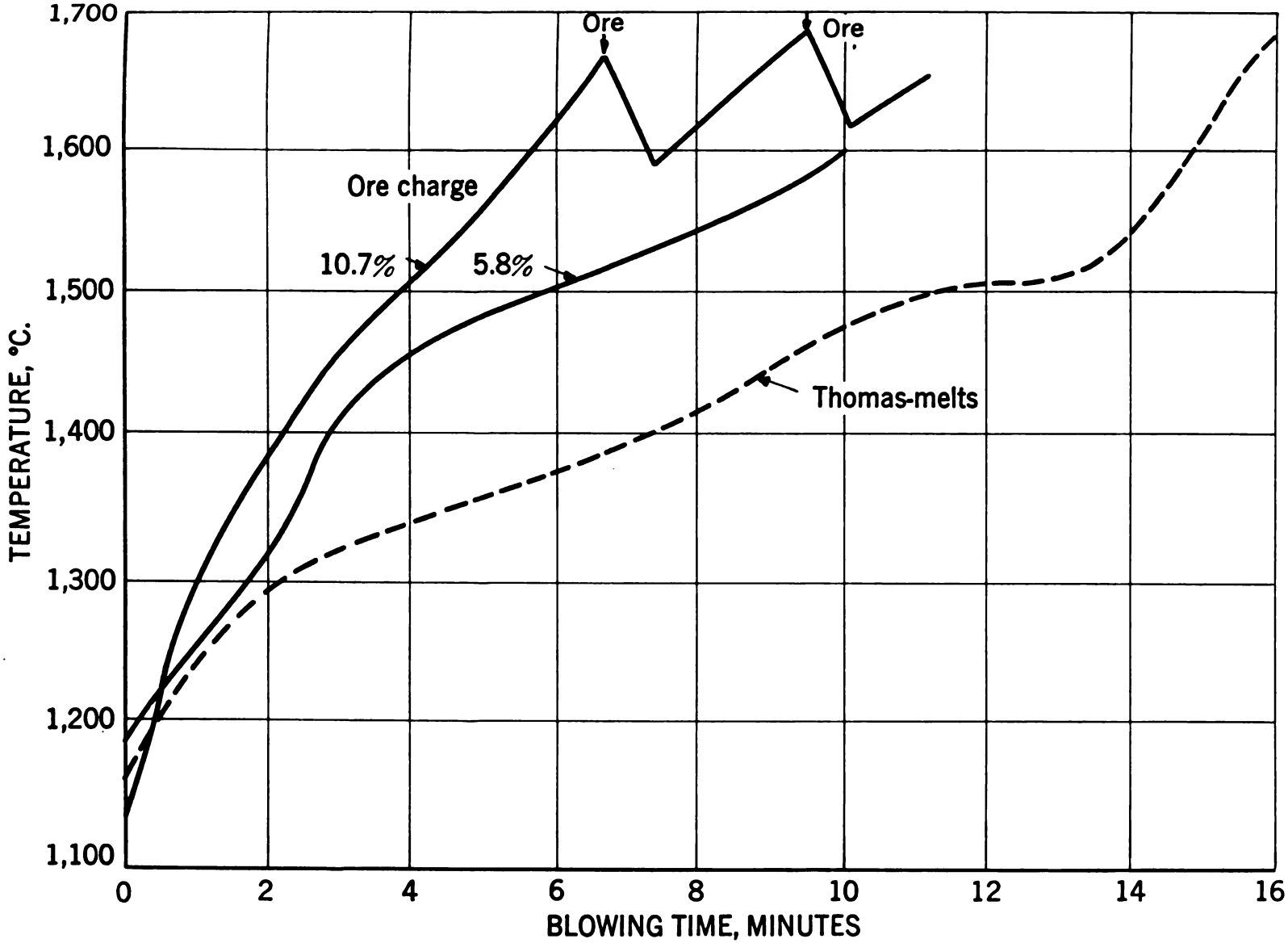

Figure 23. - Temperature changes in spiegeleisen and Thomas Basic Bessemer melts.

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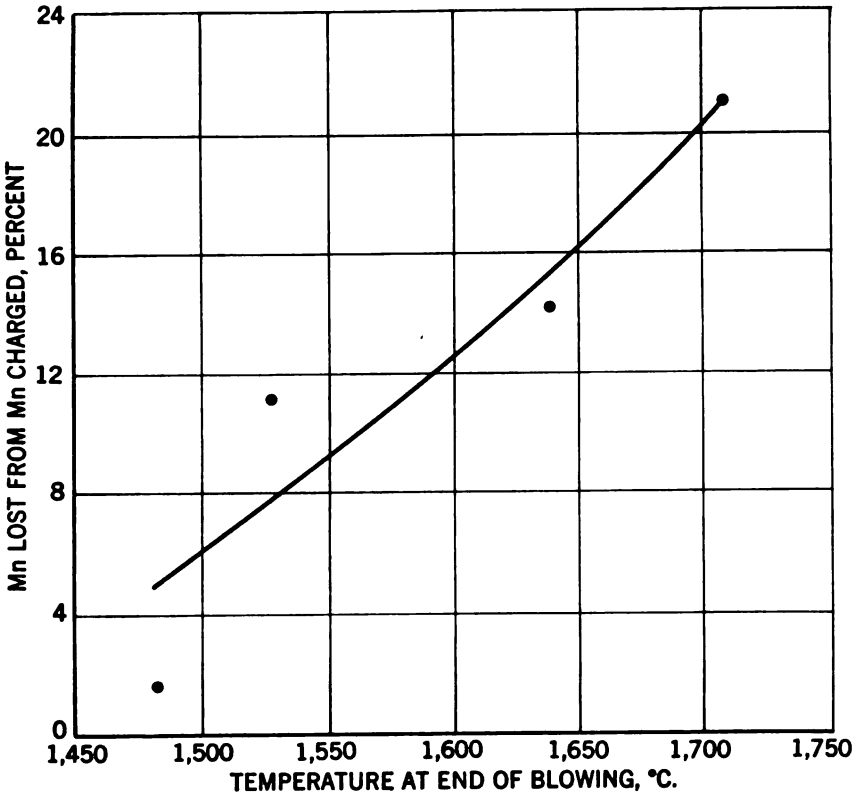

Figure 24. - Influence of temperature of blowing upon manganese loss.

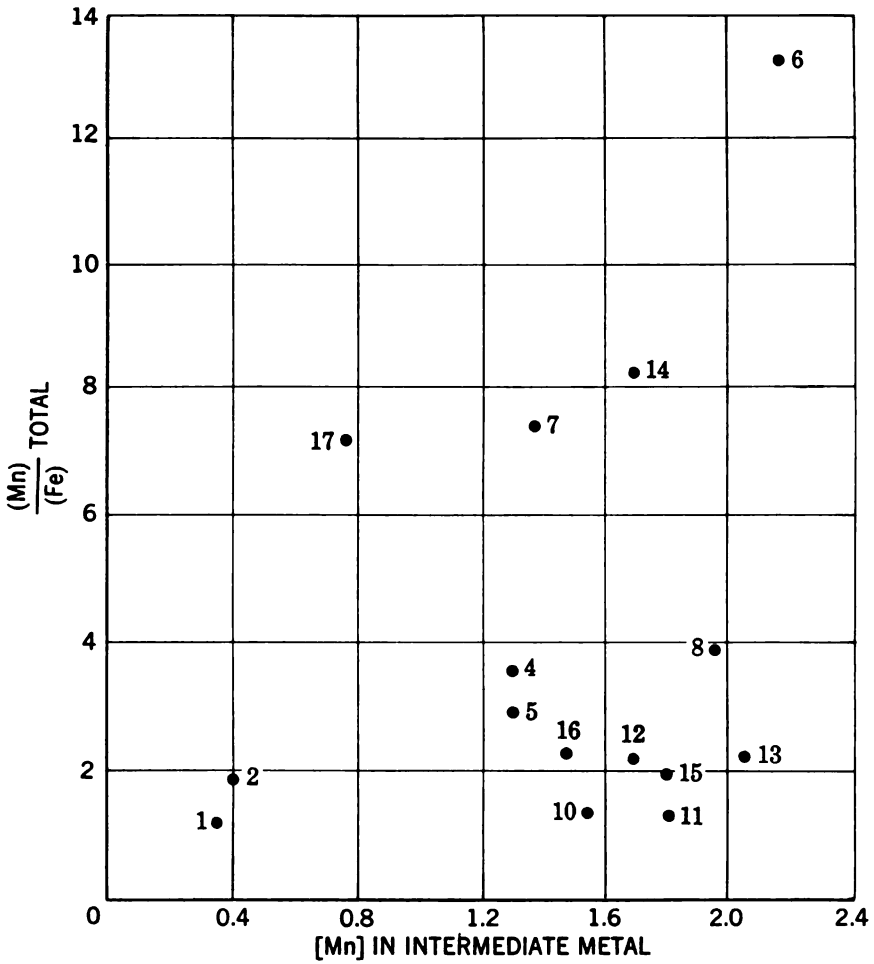

Figure 25. - Ratio of Mn:Fe in slag from blowing spiegeleisen at different plants.

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To slag the manganese at 1,350° to 1,450° C., drastic cooling is necessary. With manganese content in the pig iron under 6 percent, phosphorus spiegel and, at higher manganese contents, oxide- or silica-bearing ores may be applied as cooling agents. The cooling material charge, which is placed in the converter at the beginning, varies between 10 and 15 percent. With this strong cooling, the manganese was largely slagged before oxidation of the carbon.

The blowing times then of 3 to 5 minutes were very short. Dissolving and reduction of ore was largely incomplete in this time. However, in order to maintain slags with a lower phosphorus and iron contents, metal and slag with additions of fluorspar were emptied together into a cast-iron pan. After withdrawing the thin-fluid manganese silicate slags, the carbon- and phosphorus-bearing intermediate metal was treated in the mixer. When preparing high-manganese slags from low-phosphorus pig irons, the phosphorus content of the slag requires hardly any attention, since it is low enough. Preparation of manganese silicate slags produced no essential advantage but were a great disadvantage in the later smelting of ferromanganese. The procedure is determined by the treatment the blown intermediate metal will receive. The first possibility, treating the remaining low-phosphorus metal with spiegel at lower temperatures in the mixer changes the silicon and phosphorus content of Thomas pig iron, so that it is difficult to blow in producing steel. This is especially true when the amounts of blown spiegel and of Thomas pig iron are nearly equal.

The second possibility, that the remaining iron be blown to steel in a second converter or that the very hot intermediate iron be duplexed in the Siemens-Martin furnace (open hearth), requires temperatures of 1,650° to 1,720° C.

In the process of blowing spiegel in Hamborn, this possibility was tested. In the first tests, the intermediate metal at a temperature of 1,530° C. was treated in the mixer, whereas during later blows the intermediate metal at an average of 1,640° was finished blown to steel, and at 1,710° mainly to duplex metal to the open hearth.

The temperature rise of a spiegel melt during smelting differs, thereby, fundamentally from a Thomas (basic Bessemer) melt (fig. 23). The main rise follows, in case no large cooling material additions are used, right at the start, while toward the end of the melt no more appreciable increase occurs; the main rise in a Thomas melt, ensues after carbon removal. The influence of the amount of cooling material upon the temperature of the process and the final temperature of the melt is distinctly noticeable.

Through the various changes of temperature during the observed heats, it was found that the manganese loss, probably through vaporization of MnO, is influenced strongly by temperature (fig. 24). Whereas, under 1,500° C., losses are difficult to detect, they amount to about 20 percent at 1,700°.

An important hint to the method of manganese vaporization is given by the limestone-cooled melts. It appears that the melts with stiff and solid slags, in spite of the high temperatures, around 1,720°, smoked less than

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melts without added lime. The appearance of the well-known yellow smoke over 1,500° is strongly influenced by the degree of fluidity of the slag.

The utility of the manganese slag produced for preparing ferromanganese is distinguished by the ratio Mn:Fe (ges) (entrapped metal granules) in the slag. Only the manganese silicate slags and the pasty crumbly slags that have been processed by magnetic separation are suitable for the requirements of a manganese ore to produce a high-grade ferromanganese (fig. 25). If one believes, however, that the manganese silicate slags, because of their high silica content, will give only a poor manganese recovery on smelting in the blast furnace, then only the pasty-crumbly slags given the magnetic separation have the required quality. From the slags with a Mn:Fe ratio of 2:4, at best, only 50 percent ferromanganese can be prepared.

The converter stability on blowing spiegel did not differ with the procedure followed. Blowing spiegel at lower temperatures (1,400° to 1,500° C.) with pasty slags is not unfavorable to converter stability. At the mouth a thicker deposit forms. At higher temperatures of 1,650° to 1,700° C., there was apparently no greater determinable effect on refractories than with Thomas melts, providing the slag was pasty-crumbly. If, however, it were very far overblown, so that the slag was very high in iron and fluid, then a strong erosion started on the sides (flanken).

When blowing phosphorus-spiegel, part of the time the intermediate metal was finish blown to steel in the same converter. In this case, the final blowing also produced fluid slags with 25 percent Mn and 30 percent Fe, which strongly eroded the side lining of the converter. By finishing the blowing of the intermediate metal to steel or duplexing metal in a second converter, the attack could be decreased, since the melt could be stopped at 0.06 to 0.09 percent P, before the slag was thin. With this procedure, from the preliminary chemical sample to tap sample, there was no reversion of phosphorus, but a phosphorus drop was observed between the two metal samples.

CONCLUSIONS

No single procedure for blowing spiegel can be designated as the most applicable process. The operational procedure to be selected depends on the kind of crude metal (high or low phosphorus) and the disposition of the resultant metal (return to the mixer or finish blown to steel or duplex metal).

When blowing high-phosphorus manganese-iron alloys to attain a low phosphorus content in the slag product, it is desirable to produce a fluid high silica slag, because under such conditions the iron and phosphorus contents of slag are low, and the entrapped metal content of the slag rarely is higher than 5 percent. The Mn:Si ratio in the crude metal generally is within the range 2.5:4. The temperature is maintained at approximately 1,400 C. and blowing is continued only to the beginning of carbon oxidation. For coolants, 10 to 15 percent ore, roll scale, or phosphor spiegel may be added at the start of blowing. If entrapped metal is to be separated magnetically it is preferable to work toward pasty or crumbly slags during the oxidation of manganese. Under such conditions, the operating temperature must exceed 1,600° C. to maintain the required low phosphorus content in the slag.

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On the other hand, it is not desirable to operate with high-silica fluid slags on blowing low-phosphorus spiegel, since the phosphorus content of the slag usually is low enough and a high silica content is undesirable because of its adverse effect on manganese recovery in the blast-furnace. The most favorable crude-metal composition lies in the range 0.3 to 1.0 percent Si and 6 to 12 percent Mn. In this range, pasty or crumbly slags are to be expected. If the blown metal is to be diverted to the mixer, a temperature of 1,500° C. should be aimed for. When the bath is to be blown to finished steel or duplexed, temperatures must be brought to the 1,650° to 1,700° C. The treated metal must not be blown to lower than 1.5 to 2 percent Mn, otherwise the iron content of the slag would be too high with consequent unfavorable Mn:Fe ratio. Ore and scrap are satisfactory cooling materials. Although there is very little vaporization loss during blowing spiegel at the lower temperatures, there may be as much as 20 percent loss in weight at high temperatures. Addition of lime adversely affects the slagging of manganese and the Mn:Fe ratio in the slag. When crumbly slags are produced, the entrapped metal must be removed by magnetic separation in order to produce a standard grade of ferromanganese from the high-manganese slag product.

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